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Development Of High Strength High Toughness Third Generation Advanced High Strength Steels.

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DEVELOPMENT OF HIGH STRENGTH HIGH TOUGHNESS THIRD GENERATION ADVANCED HIGH STRENGTH STEELS

by

CODRICK JOHN MARTIS

DISSERTATION

Submitted to the Graduate School

of Wayne State University,

Detroit, Michigan

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DOCTOR OF PHILOSOPHY

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Major: MATERIALS SCIENCE AND ENGINEERING

Approved By:

____________________________________
Advisor     Date

____________________________________
Co – Advisor     Date
DEDICATION

To my father Jacob Martis
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CHAPTER 1. INTRODUCTION

Advanced High Strength Steels (AHSS’s) are those classes of materials whose mechanical properties are superior to the conventional steels. Conventional steels have yield strength values less than 300MPa and Ultimate tensile strength values less than 600MPa. Moreover in conventional steels as the strength increases the ductility, formability and the fracture toughness decreases and vice versa. AHSS’s have simultaneous high strength and high ductility along with good formability. Automotive industries played an important role in the development of the advanced high strength steels. The need for light weight auto body to improve fuel economy of the vehicles led to the design of the new generation of advanced high strength steels. These steels have high strength to weight ratio and are used as thinner gauge sheet steel to reduce the car weight and also to improve crash worthiness [1, 2].

Based on the properties, alloying additions and on the microstructures these steels are categorized into “first generation” and “second generation AHSS’s”. The first generation AHSS’s are Dual phase (DP), Transformation induced plasticity (TRIP), Complex phase (CP) and Martensitic (MART) steels. The primary constituent phases of these steels are ferrite and martensite. Dual phase steel was the first AHSS designed from conventional high strength low alloy steel [3]. DP steel is obtained by alloying the conventional high strength low alloy steel with grain refining elements and heating it to the intercritical temperature range to obtain fine grained alpha and gamma phases followed by quenching to transform austenite to martensite. Their chemical composition range is C: 0.06-0.15 wt%; Mn: 1.5-2.5 wt%; Si: 0.3-0.5; Cr & Mo up to 0.4 wt%; V up to 0.06 wt% and Nb up to 0.04 wt%. Figure 1 shows the phase diagram and processing route for the dual phase steel. The hard phase martensite imparts strength to the alloy and varying the martensite volume fraction increases the strength. DP steels contain 10-40%
volume fraction of martensite and the tensile strength range from 600 -900 MPa and the ductility is in the range of 24-30% [4-6]. TRIP steels were designed based on the concepts of DP steels. The DP steels contained retained austenite along with martensite and it was found out that the ductility of DP steels increased with increase in retained austenite content [7]. This increase in ductility was due to the strain induced transformation of austenite to martensite, which when explored in great details, gave birth to the Transformation Induced Plasticity (TRIP) steels.

TRIP steels are low/medium carbon, low alloy steels with Mn and Si as major alloying elements [9]. Their chemical composition range is C: 0.12 – 0.55 wt%; Mn: 0.20 – 2.5 wt%; Si: 0.40 – 1.8 wt%. TRIP steels have tensile strength in the range of 600-1000MPa and the ductility in the range of 26-32%. Their microstructure consists of 55-60% ferrite, 30-35% bainite and 7-15% retained austenite. They are heated to austenitizing temperature and then allowed to cool slowly in the $\alpha+\gamma$ field along with thermo-mechanical treatment to refine the grains. After obtaining the required amount of ferrite phase, the alloy is cooled rapidly to bainite.

Figure 1: Phase diagram and processing route for Dual Phase steel [8].
transformation temperature range to obtain bainite. At each stage the retained austenite gets enriched with carbon and is stabilized, which then doesn’t decompose during the final stage of cooling to room temperature [10]. Figure 2 shows the processing route for TRIP steel.

![Figure 2: Processing route for the transformation induced plasticity (TRIP) steel][10].

Complex phase steels are similar to TRIP steels in composition but also contains Nb, Ti, V to cause the precipitation strengthening. It contains more volume fractions of hard phases, martensite and bainite in fine grained ferrite matrix. The tensile strength properties of these steels are in the range of 700-1000MPa and the ductility is 10-20% [2]. Martensitic steels have very high tensile strength among the first generation advanced high strength steels in the range of 1200-1600MPa but their ductility is limited to 4-6%. These are obtained by heating the alloy to austenitizing temperature and then rapid quenching to room temperature to obtain lath martensite [2]. Dual phase (DP), TRIP and Complex phase (CP) steels have good fracture toughness, formability and absorb high energy while deforming and they are used as energy absorbing components in auto body to improve crashworthiness of the vehicle. Martensitic steels on the other hand are hard, stiff and stronger are used as a load transferring barriers for the protection of car passengers [11]. Even though first generation steels have good ductility and formability,
their strengths are not sufficient for significant weight reduction and energy savings of next generation vehicles. The second generations of AHSS’s were designed to improve the strength without compromising the formability, ductility and energy absorption of the steels.

Second generation AHSS’s are Twinning induced plasticity (TWIP), Light-weight steels with induced plasticity (L-IP) steels. These steels are highly alloyed with austenite stabilizers to obtain fully austenitic structure at room temperature [12, 13]. The major alloying element is Mn and is added in the range of 17-25% to stabilize austenite. Al and Si are also added to avoid carbide precipitation and other phase transformations. The TWIP steel has high ductility and high strain hardening behavior due to the formation of deformation twins during plastic deformation and then these twins act as a barrier for dislocation motion. The TWIP steels have tensile strength in the range of 900-1100MPa and ductility in the range of 40-70%. The difference between TWIP and L-IP steel is that latter contain high amount of Aluminum in the range of 9-10% (TWIP steels contain 2-3%Al) thereby reducing its weight up to 14% than the pure iron, hence the name light weight induced plasticity [14]. The addition of Al increases the stacking fault energy which prevents twin formation and the strain hardening occurs by slip activation [15]. Even though second generation AHSS have combination of high strength and ductility their processing is difficult and expensive due to the presence of large amount of Mn addition. TWIP steels are also known to show delayed cracking after they are formed.

The first generation AHSS’s have very high strength but their formability is limited to produce future generation light weight auto bodies and their high strength comes from the hard phases like martensite, bainite. Whereas second AHSS’s have combination of both high strength and ductility but they are expensive and hard to process due to the presence of large amount of alloying elements. Their strength is mainly due to the austenitic microstructure. The attempt to
increase the ductility (formability) of first generation of AHSS’s and to reduce the cost of production of second generation AHSS’s (by decreasing the alloy content) without compromising the strength, led to the exploration of new Third generation of AHSS’s. Third generation advanced high strength steels have mixture of hard phases (martensite, bainite) and austenite in the optimum amount. To achieve the higher strength than the first and second generation AHSS’s and ductility in the range between the first and the second generation AHSS’s, new processing techniques and alloy designs have been conceived. The new Quenching and partitioning heat treatment has been successful in producing high strength and ductility combination in steels by producing martensite and stable austenite [16-18]. Isothermal heat treatment of high carbon high silicon steel at 125°C produced nano-scale (∼ 20nm) carbide free bainitic ferrite and high carbon austenite [19-21]. Modified transformation-induced plasticity (TRIP) steels with high carbon and manganese content have been developed which has higher austenite fraction compared to first-generation TRIP steels [22]. Dual-phase (DP) steels strengths have been improved by obtaining higher volume fraction of martensite [23, 24].

Putatunda et. al., [25] designed medium carbon high silicon steel which when processed by austempering (isothermal) heat treatment resulted in carbide free bainitic ferrite along with stable austenite. The obtained microstructure imparted high tensile strength in the range of 1354-1779MPa and the fracture toughness in the range of 70 -116 MPa√m, to the steel. This steel when processed via two step austempering resulted in higher tensile strength in the range of 1381-1961MPa and fracture toughness in the range of 74-99MPa√m [26]. The current investigation is focused on designing a low carbon – low alloy (LCLA) steel combined with single step and two step austempering heat treatment to obtain exceptional combination of high strength and toughness.
CHAPTER 2. LITERATURE REVIEW

2.1 Microstructures of the advanced high strength steels (AHSS’s)

First generation advanced high strength steels have predominantly ferrite and martensite microstructure along with little amount of retained austenite. The strength and ductility of the steels are enhanced based on the adjustment of volume fractions of soft phase ferrite and the hard phase martensite [27]. Little amount of retained austenite present in the first generation AHSS (10-15% in TRIP steels) transforms to martensite while loading thereby increasing the toughness by transformation induced plasticity (TRIP) effect [28]. Second generation advanced high strength steels have completely austenitic microstructure and the high strength and toughness are obtained by TWIP effect (Twinning induced plasticity) [14]. To develop future generation AHSS’s microstructures, Matlock et al. [29, 30] developed a composite model to predict the combination of elongation and tensile strengths of the hypothetical mixed microstructures. From the assumed properties of the constituent phases, final predicted properties of the mixed microstructures are superimposed on elongation - tensile strength plot of current first and second generation AHSS’s. It was found that the predicted property combination of ferrite + martensite microstructure match that of first generation advanced high strength steels and the predicted property combination of the martensite + austenite microstructure lie in the property gap between the first and second generation AHSS’s (figure 3). Matlock et al. [30] also considered the stability of austenite in their model to predict its effects on the properties. Stability of austenite is with regard to the strain induced transformation. If the retained austenite is not sufficiently enriched with carbon it transforms to martensite at lower strains during loading and the transformed hard martensite embrittles the steel [31, 32].
Figure 3: Superimposed predicted combination of properties of hypothetical mixture of constituent phases [30].

Figure 4 shows the four hypothetical stability conditions for austenite which illustrates the transformation to martensite with respect to true strain. Condition ‘A’ being the highly stable austenite where higher strains are required to transform austenite to martensite and ‘D’ is the least stable austenite condition [30]. Their prediction of combination of properties using these hypothetical conditions gave a better understanding of the effects of individual constituent phases. Significant amount of hard phases martensite, bainite and ultrafine ferrite along with ductile stable austenite microstructure is needed to obtain third generation advanced high strength steels.

Figure 4: Volume fraction of austenite transformed to martensite with respect to the true strain (austenite stability) [30].
2.2 Overview of Bainite

Pioneering work on isothermal transformation of steels by Davenport and Bain [33] led to the identification of the new phase Bainite in late 1920’s. Bainite phase is formed from the austenite phase in the temperature region below the pearlite transformation temperature but above the martensite start ($M_s$) temperature. Bainite is a nonlamellar mixture of ferrite and cementite unlike pearlite. This is a general definition of bainite but due to the difficulty in understanding the mechanism of bainite formation various other definitions are found in the literature [34-38]. Bainite forms in the temperature range of 250 to 550$^\circ$C and this range varies depending on the composition of the steels [39]. In this temperature range, bainite appear in two forms, upper bainite and lower bainite. Upper bainite forms in the temperature range of 400 - 550$^\circ$C and the cementite is precipitated in between the bainitic ferrite plates or laths. Whereas lower bainite forms in the temperature range of 250 -400$^\circ$C and the cementite is precipitated inside the lower bainite laths or plates along with precipitation between the laths or plates of bainitic ferrite [40]. But in some steels, close to the transition temperature both upper bainite and lower bainite can form together [41]. Figure 5 illustrates the two forms of bainite showing the precipitation of carbides in between the ferrite plates in upper bainite and within ferrite plates in lower bainite.

![Figure 5: Schematic representation of Upper and lower bainite](image-url)
Presence of carbide precipitates in bainite makes it a hard phase and the hardness of the bainite can be compared with tempered martensite in steels [43]. But the presence of carbide is also detrimental to the mechanical properties and especially to the toughness.

2.3 Morphologies of bainite

The plates or laths of ferrite in bainite or the bainitic ferrite are called subunits and these subunits grow to a limiting size and the new subunits are formed at the tip of the previous one [44]. Aggregates of several subunits make up a sheaf. These sheaves of bainite look like needles under the optical microscope but when looked under the electron microscope clear bainitic ferrite subunits are seen separated by films of interlath carbides. Both upper bainite and lower bainite result in sheaf like morphology when isothermally heat treated. There are other morphologies of bainite such as granular bainite, inverse bainite and columnar bainite. The granular bainite is found in low carbon steels which are continuously cooled [45]. As the name suggest the bainite appear coarse and granular under optical microscope but when looked under the electron microscope it shows the sheaf morphology. Inverse and columnar bainite forms in hyper eutectoid steels. In Inverse bainite cementite forms first from the austenite phase as a leading phase and the ferrite forms as a secondary reaction [46]. Columnar bainite is same as conventional bainite but the morphology of the ferrite is like elongated colony and hence the name [47].

2.4 Incomplete reaction phenomenon

Below the bainite start ($B_s$) temperature as the temperature decreases bainite volume fraction increases. But when the steels are isothermally held at a temperature in the bainitic region, the volume fraction of bainite increases with respect to time and reach a limiting maximum value. The remainder austenite does not transform further as the time progress. This is
referred as incomplete reaction phenomenon and it is observed in alloys steels [48]. The amount of untransformed austenite increases as the isothermal hold temperature increases and reach close to the B_s start temperature and it is dependent on the alloy composition [49]. Zener [50] tried to describe with the help of thermodynamic analysis the growth of bainite and the incomplete reaction phenomenon. He assumed that the bainitic ferrite growth is diffusionless and the ferrite is supersaturated with carbon. Carbon later escapes to the surrounding austenite from the grown bainitic ferrite plate during the isothermal hold. The next plate of bainitic ferrite should nucleate from the surrounding high carbon austenite. Figure 6 shows the Ae_1 and Ae_3 curves of equilibrium carbon concentration of ferrite and austenite phases respectively. Equilibrium carbon concentrations of ferrite and austenite phases at temperature T_1 are obtained by drawing a common tangent to the free energy curves of ferrite and austenite as shown. Similarly at a given temperature T_1, the point of intersection of free energy curves gives the carbon concentration limit of austenite for the diffusionless transformation. When the carbon concentration of austenite is below this point the diffusionless growth of ferrite is thermodynamically possible as ΔG is negative.

Figure 6: Illustration of T_o curve on the phase diagram using the free energy curves of ferrite and austenite phases [42].
But as the austenite concentration increases above this point then the diffusionless growth is not possible. The locus of points on the temperature versus carbon concentration in austenite gives the $T_o$ curve and when the austenite surrounding the bainitic ferrite plate gets enriched with carbon and reaches $T_o$ concentration, the bainitic reaction stops. Zener explained this could be the reason for the incomplete reaction phenomenon. $T_o'$ is the curve obtained by considering the stored energy of ferrite due to diffusionless transformation [51] shown in figure 6.

### 2.5 Nucleation and growth theory of bainite

Two theories have been proposed to explain the nucleation and growth process of bainite [44, 52]. The first theory is based on the diffusionless growth of bainite proposed by Bhadeshia [44] according to this theory, bainitic ferrite nucleus grows with carbon supersaturation. The trapped carbon later partitions to the austenite. The second theory is proposed by Aaronson [52] based on the diffusion-controlled process. According to this theory the bainitic ferrite grows by the propagation of ledges (steps on the transforming interface). Due to the difficulty in the nature of bainite formation and its fast growth rate both the theories have some unanswered issues [53]. Here only diffusionless theory is reviewed and used to compare the observed results.

According to the diffusionless theory the nucleus of bainitic ferrite is a stacking fault which is formed by disassociation of partial dislocation (similar to martensite nucleus) [54]. This then grows into a plate when the driving force is sufficient. Bhadeshia showed that the nucleation activation energy ($G^*$) is linearly proportional to the chemical driving force $\Delta G_{CHEM}$ (change in free energy of transformation from parent to the product phase) [55]. As the $\Delta G_{CHEM}$ increases the nucleation activation energy ($G^*$) decreases linearly whereas for diffusional process there is inverse square relationship between the two. Bhadeshia observed that the TTT diagram of the alloy steels show two C curves, one for the diffusional ferrite and pearlite transformation and
other for the bainite and widmanstatten ferrite. The widmanstatten ferrite and bainite C curve shows a flat top and above this temperature the bainite or widmanstatten ferrite doesn’t form. This temperature is referred as $T_h$. Based on the surface relief observed and the crystallography of widmanstatten ferrite, Bhadeshia concluded that the growth is displacive but the carbon partitions during growth [56]. He considered that the widmanstatten ferrite and bainitic ferrite has the same nucleus but grows into different morphology based on the prevailing thermodynamic conditions. He then calculated the maximum possible free energy change $\Delta G_m$ for the nucleation at $T_h$ for large number of steels. The figure 7 shows the free energy change necessary for nucleation of widmanstatten or bainite at $T_h$ and each data point refers to different steel. From these plots it is concluded that the carbon partitions during nucleation, since the free energy change calculated assuming no change in composition ($\Delta G_{\gamma\rightarrow\alpha}$), resulted in increase in free energy as shown in figure 7(b). And to determine the $T_h$ for any steel the data in figure 7 (a) was fitted with a line and this is referred as universal nucleation function ($G_N$) and is given as

Figure 7 The free energy change necessary nucleation of bainitic or widmanstatten ferrite at temperature $T_h$ a) calculated assuming partitioning of carbon during nucleation b) calculated assuming no change in composition during nucleation [55].
$$G_N = C_1(T - 273.18) - C_2 \quad \text{J mol}^{-1} \quad (1)$$

Where $C_1 = 3.637 \pm 0.2 \text{ J mol}^{-1} \text{ K}^{-1}$ and $C_2 = 2540 \pm 120 \text{ J mol}^{-1} \text{ K}^{-1}$ for the temperature range of 670-920K [57]. This equation gives the minimum change in free energy required for nucleation for any steel at temperature $T$. For the nucleation to occur

$$\Delta G_m < G_N \quad (2)$$

Once the stable nucleus is formed, it has a barrier to overcome. Both the widmanstatten and bainitic ferrite form by displacive mechanism and they give rise to strain energy due to the shape change. Bhadeshia calculated this stored energy for both widmanstatten and bainitic ferrite and it was 50 J mol$^{-1}$ and 400 J mol$^{-1}$ respectively [55]. Even though the widmanstatten ferrite growth is displacive, the carbon is partitioned to the austenite during the growth under paraequilibrium condition [58]. Paraequilibrium is a condition where the iron to substitutional solute atom ratio (Fe:X, where x is solute atom) is same across the interface (i.e., in parent and product phase) and only the interstitial atoms are diffused across the transforming interface due to the difference in chemical potential. The nucleus will grow into widmanstatten ferrite if the change in free energy ($\Delta G^{\gamma \rightarrow \gamma' + \alpha}$) during the decomposition of austenite into widmanstatten ferrite and high carbon austenite under paraequilibrium condition is

$$\Delta G^{\gamma \rightarrow \gamma' + \alpha} < -G_{SW} \quad (3)$$

Where $G_{SW}$ is the stored energy of widmanstatten ferrite which is 50 J mol$^{-1}$. At $T_h$ if both these conditions, $\Delta G_m < G_N$ for nucleation and $\Delta G^{\gamma \rightarrow \gamma' + \alpha} < -G_{SW}$ for growth, satisfy then the $T_h = W_s$ widmanstatten start temperature. In this case bainite will form below $W_s$ at larger undercooling to overcome the bainitic ferrite stored energy (400 J mol$^{-1}$) barrier and when the change in free energy ($\Delta G^{\gamma \rightarrow \alpha}$) during the transformation of austenite to ferrite with no change in composition is

$$\Delta G^{\gamma \rightarrow \alpha} < -G_{SB} \quad (4)$$
- then the nucleus will grow into bainitic ferrite plate or lath with carbon supersaturation. Where $G_{SB}$ is the stored energy of bainitic ferrite which is 400 J mol$^{-1}$. If at $T_h$, $\Delta G_m < G_N$ and $\Delta G^{\gamma\rightarrow\alpha} < -G_{SB}$ then the $T_h = B_s$ and the flat top correspond to the bainite start temperature and the widmanstatten ferrite will never form in the steel. Figure 8 shows the calculated change in free energies of transformation versus temperature for the example steel to determine the widmanstatten and bainite start temperatures.

![Graphical solution for the determination of $B_s$ and $W_s$](image)

Figure 8: Graphical solution for the determination of $B_s$ and $W_s$ [59].

From the figure, at around 525°C $\Delta G_m$ or $\Delta G_{Max}$ crosses the universal nucleation function straight line and below this temperature $\Delta G_m < G_N$. It should be observed that the free energy change ($\Delta G^{\gamma\rightarrow(\gamma+\alpha)p}$) for growth of widmanstatten ferrite is sufficient to overcome the stored energy barrier above 525°C but nucleation is not possible ($\Delta G_m > G_N$) above this temperature and the widmanstatten will form only below 525°C (as shown in figure 8). The bainitic ferrite nucleation is possible (since $\Delta G_m < G_N$) below 525°C but the change in free energy ($\Delta G^{\gamma\rightarrow\alpha}$) curve for diffusionless growth crosses the stored energy barrier of $-G_{SB}$ at around 480°C and hence the bainite start ($B_s$) and widmanstatten ferrite start ($W_s$) temperatures are 480 and 525°C.
respectively. There is a good agreement between the experimental values and the predicted start $B_s$ and $W_s$ temperatures using the diffusionless theory [59]. Based on this Bhadeshia developed model for kinetics of bainite transformation by relating the nucleation rate to activation energy ($G^\ast$) needed for nucleation which is intern related to the $\Delta G_m$. The nucleation rate is given by

$$I_v \propto v \exp\left\{\frac{-G^\ast}{RT}\right\}$$

(5)

The rate equation and the detailed kinetic theory model gives the time required for the formation of certain volume fraction of bainite [54]. Over the year this model has been improved and modified by many researchers [60-62]. Matsuda and Bhadeshia model [62] considers that the bainitic ferrite nucleates at the grain boundary and as the plate grows the shape change introduces the plastic deformation in austenite which results in incoherency between the interface of bainitic ferrite and austenite. This result in the limiting size of the bainitic ferrite subunits and the new plates grow at the tip of the existing plates by sympathetic nucleation [44]. Models also consider the change in thermodynamic parameters $\Delta G_m$, $\Delta G^{\gamma\rightarrow\alpha}$ as the austenite gets enriched due to carbon partitioning from the existing plates, at each time step of the calculations. Total volume fraction of bainite transformation is obtained using the model by giving chemical composition, grain size, time and temperature as the input parameters. All the above models uses the thermodynamic parameters ($\Delta G_m$, $\Delta G^{\gamma\rightarrow\alpha}$ and $x_{To}$), obtained from the chemical composition using the thermodynamic analysis of isothermal transformations developed by Bhadeshia [63].

The above explained diffusionless theory does not consider the effect of carbide precipitation during the bainite transformation. This theory was developed during the study of bainite transformation in high silicon steels [32, 64, 65]. It is determined that the addition of Si more than 1.5wt% to the steel results in the suppression of cementite precipitation during bainite
and the microstructure results in bainitic ferrite along with thin films of high carbon austenite [65]. Reasonable good agreement has been observed between the predicted and experimental values of volume fractions of bainite and also the carbon content in austenite at the termination of bainite reaction (i.e, \(x_{T_0}\)) for high silicon steels [21, 66-68]. Using the \(T_o\) concept the maximum possible volume fraction of bainite is given by [44]

\[
V_{b, \text{Max}} = \frac{x_{T_0} - \bar{x}}{x_{T_0} - x^\alpha} \quad (6)
\]

where \(x_{T_0}\) is the carbon concentration in austenite corresponding to the \(T_o\) curve, \(\bar{x}\) is average carbon concentration of the alloy and \(x^\alpha\) is the paraequilibrium carbon concentration in ferrite. This maximum volume fraction calculation assumes that there is no cementite precipitation occurring within the ferrite laths and in the austenite during the bainitic growth. Also model assumes that there is no other transformation occurs during bainite growth (ex. Martensite or pearlite).

Santofimia et al. [69] evaluated the diffusionless theories [60-62] and validated for the two types of steel with almost similar alloy content except for the silicon content. One alloy contained high silicon (1.48 wt%) and other alloy had the low silicon content (0.28 wt%). They found out that for the low silicon steel the predicted kinetics of transformation was slower compared to the experimentally observed kinetics. The experimentally observed volume fractions were higher than the predicted values for the low silicon steel. For high silicon steel, reasonable good agreement was observed between the predicted and measured volume fractions, but the predicted kinetics were faster than the experimentally observed kinetics. They concluded that the precipitation of carbon in low silicon steel resulted in depletion of carbon in austenite which resulted in further formation of bainitic ferrite. Nonetheless, diffusionless theory played an important role in developing the high strength high toughness carbide free bainitic steels.
2.6 Carbide free bainitic steels

The two carbide free silicon steels developed by Bhadeshia and Edmonds [32, 64] were further investigated for mechanical properties by Miikinen and Edmonds [70-72]. They obtained strengths in the range of 1375-1440MPa and fracture toughness of 160MPa√m in Fe-0.2C-2Si-3Mn steel isothermally heat treated at 250°C. These properties were comparable to quench and tempered steel AISI 4340 steel [71, 72]. Ever since, improved carbide free bainitic steels have been designed based on the diffusionless theory of bainite transformation. The key feature in designing these steels is the $T_o$ curve as pointed out by Bhadeshia and Edmonds [44]. They pointed out that by lowering the overall carbon content of the steel results in the higher volume fraction of bainite. Since the carbon content of austenite reaches $x_{T_o}$ at the later stage of transformation. But this is only useful if the reduction in carbon content does not result in decrease in the strength of the steel. The other method of increasing the volume fraction of bainite is by shifting the $T_o$ curve to the higher carbon content by adding suitable alloying additions.

Isothermally heat treating the steel at the lowest temperature in the bainitic region but just above the $M_s$ temperature results in the maximum volume fraction of bainite compared to the higher isothermal temperatures. At lower isothermal temperatures, the fraction of blocky austenite reduces due to the maximum fraction of austenite transforming to bainite.

Caballero et al [67, 68] improvised the Bhadeshia and Edmonds high silicon steels by decreasing the silicon content from 2 to 1.5wt% which was sufficient to suppress the cementite precipitation. Manganese content was decreased from 3 to 2wt% and their calculation showed that it shifted the $T_o$ curve to the higher carbon content. They also added 1.44wt% Cr to improve the hardenability which resulted in $T_o$ curve shifting to lower carbon content. And the Ni content
was reduced from 4 to 3.5 wt% and carbon content of both steels was kept at 0.3 wt%. Instead of isothermal heat treatment they were air cooled in the bainite region by avoiding the nose of the ferrite C curve. The Ni2 (Fe-0.3C-1.5Si-1.44Cr-0.25Mo-3.5Ni) alloy resulted in highest volume fraction of 81% and retained austenite of 11% and remainder was martensite. Exceptional combination of yield strength (1100 MPa), tensile strength (1625 MPa) and ductility (14%) was obtained in this steel. Caballero et al. [73] designed new steels based on Ni2 alloy for the automotive application and their chemical compositions are reported in table 1. They had similar carbon, silicon and molybdenum content but the Mn, Ni and Cr content were varied as reported in table 1.

**Table 1: Chemical compositions of designed carbide free bainitic steels [73].**

![Chemical compositions of designed carbide free bainitic steels [73].](image)

**Figure 9: a) T₀ curve, b) TTT diagram of designed carbide free bainitic steels [73].**
Figure 9 a) shows the $T_o$ curves for the designed steels and the combination of alloying elements were purposefully chosen such that they resulted in almost similar $T'_o$ and same maximum volume fraction of bainite. Figure 9(b) shows the TTT diagram of these steels and the diffusionless paradigm (the bainitic region, $B_s$ and $M_s$) was same for all the designed steels whereas their diffusion controlled C curves were different. Ni2 alloy had 3.5wt% Ni and 1.44wt%Cr which resulted in shifting of the C curve to the right compared to other alloys indicating good hardenability. Bain4 alloy had 1.47wt% Ni along with 1.53wt% Mn and it has significant hardenability as shown in figure 9 (b). These alloys were hot rolled above 900°C and then accelerating cooling up to bainitic region by avoiding diffusional C curve and then air-cooled from the respective initial quench temperature [73]. All these steels resulted in yield strength in the range of 999-1339MPa and the ductility in the range of 16-25% which makes them third generation advanced high strength steels. The comparison of first generation yield strength–ductility combination with the carbide free bainitic steels is shown in figure 10.

![Figure 10. Comparison of yield strength and ductility with the first generation advanced high strength steels [73].](image-url)
Garcia-Mateo et al. [20] developed high carbon steel with high silicon content (Fe-0.98C-1.46Si-1.89Mn-1.26Cr-0.26Mo-0.09V) with the help diffusionless theory. Due to the high carbon content the bainitic region was in between 125-325°C. This steel when isothermally heated at 125°C took 60 days to complete the bainite transformation. At 200°C it took 9 days to finish the bainite transformation and around 70% volume fraction of very fine nano scale (≈20nm) bainitic ferrite was obtained, remainder being the high carbon stable austenite. Even though the carbon content was so high and temperature so low, the carbides are not precipitated within the very fine bainitic ferrite. They theorized that the carbon is trapped at the defects instead of precipitating as carbides [20]. Hardness of the steel heat treated at 200°C was around 600HV. Due to the longer (days) isothermal hold, the application of this steel is limited and Garcia-Mateo et al. [74] added Al and Co to this steel to accelerate the bainitic reaction and they were successful in reducing the isothermal hold time from days to hours. The diffusionless theory has also been applied for commercial applications such as seamless pipes and bearings [75-77] where the continuous cooling of carbide free bainitic steels have been explored to replace quench and tempered alloys.

2.7 Quenching and Partitioning

Quenching and partitioning is a heat treatment process in which steel is quenched to a temperature between the martensite start (M_s) and finish temperatures (M_f) and isothermally held for the specified time at the initial quench temperature or above it. Speer et al [78] proposed this technique to stabilize the retained austenite. Initial quench result in martensite and during the isothermal hold carbon partitions into the austenite from the supersaturated martensite plates. Hence the name quenching and partitioning to differentiate it from traditional quench and tempering process. In traditional quench and tempering process the steel is quenched below the
martensite finish temperature and very less amount of austenite fraction is present and when the steel is tempered austenite decomposes to cementite. Quench and partitioning technique was mainly designed for alloys which has carbide suppressing elements such as Si and Al. The presence of these elements retards the cementite precipitation during isothermal hold which helps the carbon enrichment of austenite. Speer et al [78] developed a model to predict the carbon concentration at the end of portioning process through thermodynamic analysis. Under the assumption that the carbides doesn’t precipitate during partitioning, they calculated the final concentration in austenite using constrained paraequilibrium condition. They assumed that the martensite/austenite interface doesn’t migrate during the partitioning of carbon and hence the name constrained. In constrained paraequilibrium condition Fe/X ratio is same in both austenite and martensite phase and only the long distance diffusion of carbon is allowed. Since only the carbon diffusion is allowed and the diffusion process continues until the chemical potential or the activity of carbon is same in the both phases. Under constrained paraequilibrium condition, the free energy curves for ferrite and austenite shown in figure 11 suggest that there are infinite different possibilities of final carbon composition of carbon in ferrite and austenite. They are

Figure.11: Free energy curves for ferrite and austenite showing constrained paraequilibrium condition [78].
- obtained by drawing the tangents to ferrite and austenite free energy curves from a single point from the carbon axis as shown. To obtain a unique solution matter balance of iron and carbon was used to find the final composition of carbon in austenite and ferrite. They used chemical activities of carbon from the published thermodynamic data [79-81] and with matter balance of iron and carbon final solution of carbon concentration was obtained. Input parameters needed for this model are the initial martensite and austenite fractions and the overall carbon composition in the alloy. The initial martensite fraction at a given quench temperature was obtained by the famous Koistinen –Marburger equation [82]. This model helps to optimize the quench temperature to maximize the stable austenite volume fraction thereby obtaining superior mechanical properties.

Figure 12 illustrates the phase transformation during the Q&P process. At austenitization temperature the austenite phase inherits the overall carbon content of the alloy and at initial quench, transformed martensite is supersaturated with carbon. During isothermal hold at portioning temperature carbon diffuses into austenite enriching it. The final quenching to room temperature results in the further formation of high carbon martensite from enriched austenite.

Figure.12: Schematic diagram of the Q&P process showing the phase transformation during each step ($C_i$, $C_\gamma$, $C_m$ – carbon content in initial alloy, austenite and martensite) [16].
If the austenite is sufficiently enriched during the isothermal hold, the final quench completely retains the enriched austenite without any further transformation into martensite. The complete retention is possible when the austenite carbon content at the end of partitioning temperature should be high enough that its martensite start temperature is below room temperature. Figure 12 shows the final volume fraction of austenite retained as a function of initial quench temperature. At higher temperatures just below $M_s$ temperature the volume fraction of initial martensite is low and the austenite is not sufficiently enriched and hence large fraction of austenite is transformed to martensite during final quench. At lower temperatures even though the austenite is sufficiently enriched with carbon, high initial volume fraction of martensite results in low volume fraction of austenite. But between 175 to 200°C in figure 13 shows the highest volume fraction of retained austenite due to the carbon enrichment. The initial quench fraction of martensite is obtained using the calculated $M_s$ temperature in Koistinen – Marburger equation and using the Q&P model the enriched carbon content of austenite is determined which is shown in dashed line in figure 13. The final quench fraction of martensite is

![Figure 13: Phase fraction of final austenite as a function of initial quench temperature [16].](image-url)
-obtained by calculating the $M_s$ temperature using the enriched carbon content of austenite determined by the Q&P model and then using it in Koistinen–Marburger equation. This model doesn’t consider the partitioning of carbides and also the absence of other transformations such as bainite. But during quenching and partitioning for longer isothermal hold time martensite get auto tempered [83] and also in some alloys formation of bainite below $M_s$ temperature has been observed [84]. Also this model doesn’t address the kinetics of partitioning of carbon. Nevertheless the model led to the exploration of Q&P technique and plenty of research has been carried out to study the effect of isothermal hold time on fractions of retained austenite [85-93].

The alloy design involves adding few alloying elements to improve hardenability and Si to suppress the carbide precipitation. Mn in the range of 1.5 to 2.5 wt% is added for the improvement in hardenability. This technique enables to improve the strengths and ductility of low alloy TRIP steels with sufficient silicon content [78]. De Moor et al. [17] have designed medium carbon high silicon (1.6wt %) steel with high manganese content in the range of 3-5wt%. By varying the quench temperature and partitioning time they were to obtain exceptional combination of high tensile strength in the range of 1450 -1750MPa and ductility in the range of 11-18%. These properties are in the third generation advanced high strength steels property region shown in figure 14. Li et al [94] studied single step quenching and partitioning process on medium carbon (0.4wt%) 40SiMnNiCr steel grade, which contained 1.01wt% of Ni and 0.56wt% of Cr along with regular amount of silicon and manganese. They obtained high tensile strength of 2400MPa and ductility above 10% at a quench temperature of 180°C partitioned for 100 seconds. With low alloy content of Ni, Cr and Mo, superior mechanical properties can be obtained by Q&P technique and are comparable to the carbide free bainitic steels [67, 68, 73] which usually contain little higher amount of these (Ni, Cr and Mo) alloying elements.
2.8 Austempering

Austempering is an isothermal heat treatment process used to obtain bainite microstructure. Austempering involves heating steel to austenitizing temperature and then suddenly quenched (to avoid ferrite and pearlite formation) into molten salt bath which is maintained at a temperature between the bainite start ($B_s$) and martensite start ($M_s$) temperatures. At this temperature the steel was held for the specified time to obtain required bainitic microstructure. Austempering heat treatment is a useful technique to avoid quench cracks or thermal distortion during the quenching process. The higher temperature range of austempering process (normally 250-500°C) results in the small thermal gradients within the sample which avoids distortion or residual stresses. It is normally used to obtain good hardness using bainitic microstructures in products where the dimensional changes should be minimal during the heat treatment process. Austempering process is extensively used in ductile cast iron to obtain superior properties [95-99]. Due to the high carbon and silicon content in the ductile cast iron the bainitic reaction takes longer austempering time to obtain the maximum amount of bainitic ferrite [95]. Rao et al [96] optimized the austempering temperature and time to obtain the highest
fracture toughness in austempered ductile iron (ADI) with 3.5wt%C, 2.81wt%Si and low manganese of 0.4wt%. Highest fracture toughness was achieved by obtaining fine lower bainitic microstructure with 30% retained austenite with the carbon content of austenite above 1.8wt%. Yang et al [100] used two step austempering process to improve the properties of the ADI. At initial quench temperature the samples were held for 5 min and then the temperature of the salt bath was increased by 28°C and at second step temperature austempering was carried out for two hours. The two step process resulted in stable austenite and the mechanical properties obtained were higher compared to the single step austempered ADI.

2.9 Summary

To obtain exceptional combination of high strength and ductility, steels should consists of hard phases like martensite, bainitic ferrite and ultra-fine ferrite along with optimum amount of stable retained austenite. These microstructures can be produced by isothermal heat treatment, continuous cooling and quenching and partitioning heat treatment with proper alloy design. Both Quenching and partitioning and isothermal heat treatment techniques have been successful in producing third generation advanced high strength steels. Quenching and partitioning heat treatment has been used to enhance the properties of first generation advanced high strength steels without modification of its alloy content [101, 102]. Whereas carbide free bainitic steels developed using isothermal and continuous cooling techniques have higher expensive alloying elements Ni, Cr and Mo compared to the first generation AHSS’s [67, 68, 73]. One of the requirements for the third generation advanced steels is that it should contain low amount and less expensive alloying elements. Putatunda et al [25] designed a medium carbon (0.4wt%) high silicon steel which contained lower amount of Ni(1wt%), Cr(0.82wt%) and Mn(0.4wt%) compared to typical carbide free bainitic steels [67]. They austempered the steel for 2 hours in
the temperature range of 260-400°C which resulted in ausferritic microstructure (carbide free bainitic microstructure) and very high tensile strength (1354-1779MPa) and ductility (10-18%) combination. Even though this steel has tensile strength – ductility combination as that of third generation AHSS’s, due to its higher carbon equivalent, its application is limited in the automobile industry which demand for alloys with good weldability. Thus there was a need to reduce the carbon content to improve its application potential which motivated the current investigation. Based on the work of Putatunda et al. [25], two new alloys were designed by lowering the carbon content from 0.4wt% to 0.2 and 0.3wt%. The alloying elements were kept same in the 0.3wt%C steel but in 0.2wt%C steel they were adjusted to improve the hardenability. The amounts of alloying elements Ni, Cr and Mn were still kept low compared to the high strength carbide free bainitic steels [67, 68, 73]. These two steels were austempered or isothermal heat treated above and below the $M_s$ temperature to study the evolution of microstructure and its effect on mechanical properties.
CHAPTER 3. OBJECTIVES

The purpose of this investigation is

- To design the composition and processing of two low carbon low alloy (LCLA) steels to produce third generation advanced high strength steel (AHSS) microstructures and properties.

- To examine the influence of single step and two step austempering processes on the microstructures and mechanical properties of low carbon low alloy (LCLA) steels.

- To relate the microstructural features such as volume fractions of different phases and their lath sizes to the obtained mechanical properties.
CHAPTER 4. DESIGN OF THE STEELS

Putatunda et al. [25] were successful in designing third generation advanced high strength medium carbon steel which contained mixture of hard phases bainite, martensite and stable retained austenite. They designed the steel keeping in mind that it should contain less expensive alloying elements compared to second generation advanced high strength steels and at the same time easily processable. Their steel contained high silicon (2wt %) which resulted in very fine carbide free bainitic microstructure during austempering. Based on their results two new alloys were designed to investigate further. The first alloy was designed with the same alloying elements as that of medium carbon steel designed by Putatunda et al [25] but with lower carbon content of 0.3wt%. The alloy composition is C-0.30wt%, Si-2.0wt%, Mn-0.4wt%, Ni-1wt%, Cr-0.8wt%, Mo-0.30wt%, Cu-0.5wt%, S-0.006wt% and P-0.006wt%. Mn, Ni, Cr and Mo alloying elements were added to improve the hardenability of the steel but their amounts were low compared to the second generation AHSS and typical high strength carbide free bainitic steels [13, 15, 67]. Cu was added for the corrosion resistance purposes and Si was added to suppress the cementite precipitation. Figure 15 shows the calculated TTT (time-temperature transformation diagram) for the above mentioned composition. It was obtained using the MAP_STEEL_MUCG83 [103] program available in the materials algorithm project (MAP) library of the phase transformations group of the University of Cambridge. This program was developed using the thermodynamic model by Bhadeshia [63]. The figure 15 shows two curves, the blue one is for the diffusional ferrite pearlite transformation and the red curve for the diffusionless transformation of widmanstatten ferrite and bainite. The bainite start temperature for this steel is 526°C and the martensite start temperature is 364°C. These two temperatures were calculated based on the thermodynamic analysis of diffusionless transformation explained
in section 2.5 with the help of figure 8. Above 526°C and up to 600°C, TTT diagram predicts that there is possibility of widmanstaten ferrite transformation when isothermally heat treated. It is clear that due to the lower alloying elements of austenite stabilizers (Mn, Ni, Cr, Mo), the nose of the C curves are located at the shorter time (5 and 10 seconds respectively) indicating lower hardenability and larger initial cooling rates are necessary to avoid pearlite transformation. But it will be shown later in this investigation that the hardenability was sufficient to produce maximum possible fraction of bainitic ferrite in this steel. Based on this calculation it was decided that austempering should be carried out below 400°C to obtain maximum amount of bainitic ferrite since this temperature is in the lower region of bainite and close to martensite start temperature. Due to the incomplete reaction phenomenon higher volume fraction of austenite is retained at higher temperatures and they will be in the form of islands which have detrimental effect on properties [32].

Figure 15: Time temperature transformation (TTT) diagram for 0.3%C LCLA steel.
The austenite should be present in the form of films between the bainitic ferrite and to avoid large fractions of islands of retained austenite, austempering was carried out in the lower region of bainite to obtain maximum volume fraction of bainite. Also the time for bainite reaction to start at temperatures below 400°C is between 8 to 18 seconds (figure 15) which gives enough time to quench the samples to austempering salt baths. The martensite start temperature of the steel was also calculated using the following equations [104].

\[ M_s (^\circ C) = 512 - (453 \times \%C) - (16.9 \times \%Ni) + (15 \times \%Cr) - (9.5 \times \%Mo) + (217 \times (\%C)^2) - (71.5 \times \%C \times \%Mn) - (67.6 \times \%C \times \%Cr) \]  

The calculated \( M_s \) temperature for 0.3C steel is 363°C and it was close to the \( M_s \) temperature obtained by the thermodynamic model. Austempering time of 2 hours was chosen based on the results obtained by Putatunda et al. [25] and also austempering for longer time results in maximum fraction of bainite along with stabilization of austenite by carbon partitioning mechanisms both above and below \( M_s \) temperatures. The accuracy of the model and the martensite start equations are not discussed here but results obtained show that these predictions are reasonably good. The second alloy was designed by further lowering the carbon content to 0.2wt%. Lowering the carbon content results in decrease in hardenability and for this reason the Ni, Mn, and Cr content were increased in this steel compared to 0.3C steel. Si content was reduced from 2 to 1.7wt%. The composition of the steel is C-0.20wt%, Si-1.70 wt %, Mn-0.80 wt %, Ni-2 wt %, Cr-1 wt %, Mo-0.20wt %, Nb-0.06 wt %, V-0.06 wt %, S-0.006 wt % and P-0.006 wt. The increase in amount of Ni (1 to 2wt%), Cr (0.8 to 1wt %) and Mn (0.4 to 0.8wt%) resulted in shifting of the nose of C curve of ferrite pearlite transformation to the left side in time-temperature-transformation (TTT) diagram compared to 0.3C steel (shown in figure 16). This leads to slower cooling rates to transform bainite or martensite without the formation of
ferrite and pearlite. Small amount of Nb and V were added to refine the austenite grain size. The austenite stabilizers (Ni, Cr, Mo and Mn) have drastic effect on the ferrite pearlite C curve and the nose is shifted close to 70 seconds whereas the bainitic C curve is just shifted to 10 seconds (5 and 10 seconds for 0.3C steel). The TTT diagram in figure 16 predicts that there is no widmanstatten ferrite formation in this steel. The $M_s$ start temperature of this steel is around 371°C and it is close to $M_s$ of 0.3C steel. Hence it was decided to austemper below 400°C to obtain fine and maximum fraction of bainitic ferrite. The $M_s$ temperature obtained using equation 7 is 379°C and it was little higher than the temperature obtained by the thermodynamic model. This discrepancy can be attributed to the difference in the methodology used in the calculation of $M_s$ temperature. The equation is empirical where as the model is based on the thermodynamic data. Austempering time of 2 hours was also used for 0.2C steel based upon the same assumption explained above. Here onwards these two steels are referred as 0.2%C LCLA and 0.3%C LCLA respectively.

![Figure 16: Time temperature transformation (TTT) diagram for 0.2%C LCLA steel.](image-url)
CHAPTER 5. EXPERIMENTAL PROCEDURE

5.1. Material

The alloys were melted using a vacuum induction melting furnace with a capacity of 50 pounds. A vacuum was created inside the furnace chamber and subsequently backfilled with argon gas prior to beginning of the melting process. The molten alloys were then tapped into 102 mm (4”) square tapered copper ingot molds and allowed to solidify under vacuum. The actual chemical compositions of the as received alloys are reported in table 2 a) and b).

Table.2: Actual chemical compositions of as received steels a) 0.2%C LCLA b) 0.3%C LCLA

<table>
<thead>
<tr>
<th>Element</th>
<th>wt%</th>
<th>Element</th>
<th>wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a)</td>
<td></td>
<td>(b)</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>0.21</td>
<td>C</td>
<td>0.31</td>
</tr>
<tr>
<td>Si</td>
<td>1.59</td>
<td>Si</td>
<td>2.08</td>
</tr>
<tr>
<td>Mn</td>
<td>0.73</td>
<td>Mn</td>
<td>0.36</td>
</tr>
<tr>
<td>Ni</td>
<td>2.02</td>
<td>Ni</td>
<td>1.02</td>
</tr>
<tr>
<td>Cr</td>
<td>0.99</td>
<td>Cr</td>
<td>0.83</td>
</tr>
<tr>
<td>Mo</td>
<td>0.25</td>
<td>Mo</td>
<td>0.34</td>
</tr>
<tr>
<td>Nb</td>
<td>0.062</td>
<td>Cu</td>
<td>0.55</td>
</tr>
<tr>
<td>V</td>
<td>0.064</td>
<td>P</td>
<td>0.010</td>
</tr>
<tr>
<td>P</td>
<td>0.005</td>
<td>S</td>
<td>0.002</td>
</tr>
<tr>
<td>S</td>
<td>0.010</td>
<td></td>
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</tr>
</tbody>
</table>
After removal from the furnace and the copper molds, the ingots were heated to 1093°C (2000°F). Forging was then performed to create 2 inch thick plates and were allowed to air cool to room temperature. To further reduce the thickness, these forged plates underwent a second forging operation. The plates were again heated to 1093°C (2000°F), after which they were cross-rolled to final 1 inch thickness. Final dimension of the cross rolled plates is 152 x 152 x 25 mm (6” x 6” x 1”) and all these plates were annealed at 900°C for 1 hour. From these plates tensile and compact tension specimens were prepared according to ASTM E-8 [105] and ASTM E-399 [106] respectively.

5.2 Heat Treatment

To obtain the bainitic and martensitic microstructure the two alloys were first austenitized to completely obtain γ phase and then austempered at different temperatures above and below the martensite start temperature (M_s). Figure 17 shows the schematic diagram of the heat treatment processes for the two alloys. 0.2%C LCLA steel has undergone single step and two step austempering treatments as shown in figure 17 (a) and 17 (b). Total of 7 batches of test samples were prepared for heat treatment from 0.2%C LCLA forged plates. Each batch contained 4 cylindrical tensile and 4 compact tension test samples. Four batches of test samples were then chosen for single step austempering from 0.2%C LCLA steel and were initially austenitized at 927°C (1700°F) for 2 hours. The four batches of test samples were then quenched into a molten salt bath maintained at one of four different quench temperatures: 260°C (500°F), 316°C (600°F), 371°C (700°F), and 399°C (750°F) respectively and isothermally held for 2 hours (Figure 17(a)). Three batches of 0.2CLCLA test samples were chosen for two step austempering and after austenitizing at 927°C (1700°F) for 2 hours, they were quenched into a molten salt bath maintained at one of three different initial austempering temperatures of 260°C (500°F), 316°C
(600°F), 371°C (700°F) respectively. At the initial austempering (or quench) temperature the samples were held for 5 minutes and then the temperature of the salt bath was raised by 28°C (50°F) to the second austempering temperatures of 288°C (550°F), 343°C (650°F), 399°C (750°F) respectively.

Figure 17: Schematic diagram of heat treatment process a) 0.2%C LCLA single step austempering b) 0.2%C LCLA two step austempering c) 0.3%C LCLA single step austempering.
The samples were austempered for 2 hours at the final austempering temperatures (Two step austempering, figure 17(b)). After the austempering treatment these samples were air cooled to room temperature. The figure 17(c) shows the single step austempering treatment of 0.3%C LCLA steel. 7 batches of test samples were prepared form the 0.3%C LCLA forged plates. After austenitizing for 2 hours at 927°C (1700°F), the seven batches of test samples were quenched into a molten salt bath maintained at one of seven different austempering temperatures; 260°C (500°F), 288°C (550°F), 316°C (600°F), 343°C (650°F), 371°C (700°F), 385°C (725°F) and 399°C (750°F) respectively and isothermally held for 2 hours. Finally these samples were air cooled to room temperature. In this investigation samples heat treated below Mₘ temperature are still referred as austempered samples. They may not necessarily yield the bainitic microstructure. Since they were isothermally heat treated using salt bath and typical austempering process involve using a salt bath, the usage of term austempering below Mₘ temperature is justified.

5.3 Microstructural analysis

After heat treatment, metallographic samples (2cm x 2cm and 1mm thick) were taken from each heat treated condition. These samples were mounted using a phenolic resin with the help of hot compression mounting equipment. Silicon carbide abrasive discs of varying grit size 180 -2400 were used to grind the sample surface for the final polishing step. Final polishing was done using cloth and alumina powder (1, 0.5 and 0.3µm alumina particle size suspended in distilled water) to obtain a scratch free mirror finish polished surface. The samples were then etched with 3% nital (3ml of HNO₃ in 100ml ethanol) and observed under a JEOL JSM-6510LV-LGS scanning electron microscope and optical microscope to see the microstructure. To quantitatively analyze the volume fractions of different phases present, tint etching techniques were used. Tint etchants impart different colors to different phases and volume
fractions are determined using the image analysis technique. Three different tint etchants were used and based on their etching effects, the best one is chosen for the quantitative analysis of the phases. Le-Pera tint etchant is a mixture of two solutions. It is prepared by mixing 4% picral solution and 1% sodium metabisulfite solution in 1:1 volume ratio. 4% picral is prepared by dissolving 4g of dry picric acid crystals in 100ml of ethanol and 1% sodium metabisulfite solution by dissolving 1g of sodium metabisulfite in 100ml of distilled water. The second tint etchant is 10% sodium metabisulfite which is prepared by dissolving 10g of sodium metabisulfite in 100ml of distilled water. Third tint etchant is a step etching technique where the sample is initially etched with 4% picral solution and later in the second step it is etched again with 10% sodium metabisulfite solution. Image analysis was carried out using the image pro 6 software.

To find the overall volume fraction of retained austenite and the carbon content of austenite, X-ray technique was used. The diffraction patterns were obtained using a Rigaku rotating head anode diffractometer by using Copper Kα radiation at 40kV and 100mA. Angular 2θ ranges of 42° - 46° and 72° - 92° were selected to obtain specific diffraction peaks from ferrite and austenite phases. A scanning rate of 0.25° per minute was used to obtain the diffraction pattern. The profiles were analyzed using a JADE® software to obtain the peak positions and the integrated intensities at (111), and (220) planes of FCC austenite and (110) and (211) planes of BCC ferrite. The volume fractions of ferrite ($X_\alpha$) and austenite ($X_\gamma$) were determined by the direct comparison method using the integrated intensities of the above planes [107].

This technique can be used only when there are 2 phases present in the steel. But in these steels samples austempered in the range of 260-399°C, phases like bainitic ferrite, martensite, tempered martensite and austenite are expected to form. It is a well-known fact that martensite
has a BCT crystal structure and the c/a ratio ≈ 1.0185. BCT crystal structure has a similar allowed diffraction peaks as of BCC structure but each of these peaks are split into 2 due to the c lattice parameter (a=b≠c for BCT). This split is prominent if the c/a ratio is high. In steel c/a ratio for martensite is very low and the split is not prominent and if the martensite, bainite and ferrite to coexist, then the peak intensity includes the reflection from all these phases. The main purpose of this x-ray technique was to calculate the volume fraction of austenite. Hence the bainite and martensite phases are considered as one phase and austenite as the second phase in these calculations. Therefore the volume fraction of these phases can be obtained from the ratios of integrated intensities of diffraction peaks from these two phases. The intensity ratios are given by the following equation [108]:

\[
\frac{I_{\gamma(hkl)}}{I_{\alpha(hkl)}} = \frac{R_{\gamma(hkl)}}{R_{\alpha(hkl)}} \cdot \frac{X_{\gamma(hkl)}}{X_{\alpha(hkl)}}
\]  
(8)

where \(I_{\gamma(hkl)}\) is the integrated intensity from a given (hkl) plane from the \(\gamma\) phase and \(I_{\alpha(hkl)}\) is the integrated intensity from a given (hkl) plane from the \(\alpha\) phase; \(X_{\gamma}\) and \(X_{\alpha}\) are the volume fraction of austenite and ferrite respectively; \(R_{\gamma(hkl)}\) and \(R_{\alpha(hkl)}\) are given by the following equation for respective (hkl) peak:

\[
R = \frac{1}{\nu^2} \left[ F^2 \cdot p \cdot LP \right] e^{-2m}
\]  
(9)

Where \(\nu\) is the atomic volume of the unit cell; \(F\) is the structure factor; \(p\) is the multiplicity factor; \(LP\) is the Lorentz-Polarization factor and \(e^{-2m}\) is the temperature factor.

The lattice parameter “\(a_{\gamma}\)” of austenite increases linearly with interstitial carbon atoms. Therefore, the carbon content of austenite was determined from the following equation [109]:

\[
a_{\gamma} = 0.3548 + 0.0044 C_{\gamma}
\]  
(10)
where \( a_\gamma \) is the lattice parameter of austenite in nm and \( C_\gamma \) is the carbon in wt\%. The ferrite particle sizes (d) were determined using the well-known Scherrer equation [108]. Three samples were examined from each heat treated conditions and the average values are reported here.

### 5.4 Transmission electron microscopy

TEM analysis was carried out to confirm the presence of different phases by indexing the diffraction patterns. Thin samples having a dimension of 19.05mm \( \times \) 19.05mm \( \times \) 0.5mm, were cut from the heat treated 0.2\%C LCLA and 0.3\%C LCLA samples using a band saw. These samples were then ground to 0.1mm thickness using a 180 grit silicon carbide paper. Final polishing was done using a cloth and 0.05\( \mu \)m alumina powder solution and thickness of the samples were reduced to 75\( \mu \)m. Several 3mm diameter samples were then punched from the each 75\( \mu \)m foil to electropolish. A twin jet electropolisher set at a voltage of 27V was used to create a perforation in the 3mm discs using a 10% perchloric acid electrolyte maintained at -30\degree C using liquid nitrogen. These samples were then examined near the perforated area using a JEOL 2010 (LaB6 Filament Gun) transmission electron microscope at 200kV operating voltage.

### 5.5 Tensile testing

From each heat treated condition four cylindrical samples were used for tensile testing as per ASTM standards E-8 [105]. Tensile tests were performed on a servo-hydraulic MTS system at a constant strain rate of \( 4 \times 10^{-4} \text{ s}^{-1} \). Load versus displacement plots obtained from the tensile tests were used to calculate the 0.2\% yield strength, ultimate tensile strength, \% elongation, and strain hardening exponent values. Since all of the test plates were forged, cross-rolled, and annealed in order to obtain isotropic and homogeneous properties in the material, the mechanical properties measured were not dependent on the sample reference orientation or loading direction.
Figure 18 shows the cylindrical specimen dimensions in millimeters. Average values of these samples are reported here and the statistical analysis was carried out on the obtained data using student t-test with a confidence interval set at 95%.

![Figure 18: Cylindrical tensile sample dimensions (mm).](image)

5.6 Fracture toughness

Four compact tension specimens were used from each of the heat treated condition for fracture toughness testing as per ASTM standard E-399 [106]. Fatigue pre-cracking was carried out on all of the compact tension samples to obtain a 2 mm sharp crack front using a ΔK level of 20MPa√m with a load ratio of R=0.10. The pre-cracked samples were then loaded in tension using a MTS testing machine. The clip gauge was placed in the knife-edge attachment to obtain load versus displacement plots. Using the 5% secant deviation technique, P_Q values were determined. Using the standard stress intensity factor calibration function for the compact tension specimens, K_Q values were calculated using the P_Q values. Since all of the K_Q values satisfied the requirements for a valid K_{IC} test as per ASTM E-399 [106], the K_Q values are also valid K_{IC} values. Figure 19 shows the compact tension specimen dimension and thickness of all the compact tension samples was 0.745 inch (18.9mm).
Figure 19: Compact tension specimen dimensions (Inches).
CHAPTER 6. RESULTS AND DISCUSSION

6.1 Microstructure

Figure 20 shows the as received microstructure of 0.2%C LCLA steel etched with 3% nital. The ferrite ($\alpha$) phase appears as white and the pearlite phase appears as black. The steel is a hypoeutectoid steel and the ferrite phase is also called as proeutectoid ferrite. Pearlite phase is a mixture of ferrite and cementite ($\text{Fe}_3\text{C}$) in the form of lamellar structure (alternative layers of ferrite and cementite). Figure 20(b) shows the magnified SEM image of the pearlite phase and here cementite appears as white and ferrite appears as gray is seen in the form of alternate layers.

0.3%C LCLA is also a hypoeutectoid steel and the similar as received microstructure is seen in figure 21(a) and 21(b). The microstructure shows the presence of proeutectoid ferrite which appears as white and the pearlite phase which appears as black. High magnification optical
microscope image (figure 21(b)) shows the lamellar structure of the pearlite. Comparing the figure 20(a) and 21(a), it is evident that the 0.3%C steel has a higher volume fraction of pearlite compared to 0.2%C steel. This was confirmed by the volume fraction analysis of the as–received microstructures of these two steels by image analysis. 40.9 and 45.8% volume fraction of pearlite was found with the standard deviation of 1.5 and 1.2 in 0.2 and 0.3%C LCLA steels respectively.

![Microscope Images of Pearlite](image)

Figure.21: As-received microstructure of 0.3%C LCLA steel. a) Optical microscope image (Mag 200x) b) Optical microscope image (Mag 1000x). α: Pro-eutectoid Ferrite, P: Pearlite.

### 6.1.1 Tint Etchants

Nital etchant is useful to differentiate less complex phases ferrite and pearlite in majority of the steel samples. It is hard to differentiate bainite and martensite using nital etchant due to their fine nature and similar morphological features. Austempering heat treatment carried out in this investigation yield bainite, martensite, tempered martensite and austenite phases in the steel samples. To differentiate these phases etching was carried out using tint etchants to impart color-
Figure 22: Optical micrographs of 0.3%C LCLA sample austempered at 399°C etched with a) Le-Pera solution, b) 4% Picral and 10% sodium metabisulfite, c) 10% sodium metabisulfite d) 3% Nital.
-contrast. Three standard tint etchants were chosen for etching the same sample and based on the observed results; the best etchant was used for further analysis of the microstructures. Figure 22 (a) – (d) shows the microstructure of the sample austempered at 399°C etched with LePera solution, step etching technique with 4% picral and sodium metabisulfite, 10% sodium metabisulfite and 3% nital respectively. Figure 22 a) shows the phases with dark blue, brown and white colors. This sample was immersed in the solution and oscillated for 20 -30 seconds and then rinsed with alcohol and hot air was blown to dry the sample surface. The LePera (4% picral + 1% sodium metabisulfite in 1:1 ratio) solution imparts dark blue color to the ferrite phase, brown color to bainite and white color to martensite and austenite [110, 111]. The drawback of this etchant is that it doesn’t differentiate martensite from austenite. Figure 22 b) microstructure was obtained by step etching technique which involves etching the sample with 2 etchants. First it is etched with 4%picral (4g dry picric acid in 100ml ethanol) for 60 seconds with sample immersed in the solution and oscillated for the entire duration. After the etch the sample surface was dried using alcohol and hot air. In the second step it was etched with 10% sodium metabisulfite solution for 15-20 seconds and the surface was dried in the same manner as described above.

The figure 22 b) shows dark black etched area with light blue color and white colored regions. The color contrast in this microstructure is not prominent. The 4% picral attacks the boundary between carbides and ferrite and appears as dark. In the first step phases like bainite, pearlite and tempered martensite can be easily identified [110]. The sodium metabisulfite makes martensite to appear as straw colored phase and austenite as white. Since the steel used in this investigation had high silicon content and the bainite phase was believed to be carbide free the microstructure obtained using this technique didn’t provide the proper color contrast to
quantitatively analyze the phases. Figure 22 c) shows phases with three distinct colors blue, brown and white. When the sample is etched with 10% sodium metabisulfite, bainite appears as blue, martensite and tempered martensite as brown and austenite as white color. The sample was immersed in the solution and oscillated for 30 – 60 seconds and the surface was dried with alcohol and hot air. Due to these distinct colors it is easier to find the volume fraction of these phases using image analysis techniques. Figure 22 d) microstructure was obtained by etching the sample with 3% Nital (3ml of HNO₃ in 100ml ethanol) solution. The sample was etched for 10-15 seconds by immersing it in the solution and the etched surface was dried immediately using the alcohol and hot air. Nital doesn’t produce any tinting effect and it attacks grain boundary between the two phases. Bainite etches to a greater degree than the martensite and appears dark but the contrast is not sufficient to do quantitative analysis using image analysis techniques. Nital is a very useful etchant to study the microstructure under scanning electron microscope. It is used in this investigation to differentiate the bainite and martensite based on the morphology differences between these phases using high magnification scanning electron microscope images.

Among the three tint etchants, 10% sodium metabisulfite was chosen to carry out further microstructural analysis due to the distinct tinting effect on different phases. To verify whether 10% sodium metabisulfite imparts characteristic colors (blue, brown and white) to different phases, few indentation tests were carried out to study the microstructure using the optical and scanning electron microscope. Few indentations were made using the micro hardness tester on the tint etched sample surface to serve as a marker to study the same area of the microstructure under optical and scanning electron microscope. Figure 23 shows the comparison of the microstructure of the 0.3%C LCLA sample austempered at 399°C obtained by optical and scanning electron microscopes. As pointed out in the figure, the area with blue color (image on
Figure.23: SEM and optical microscope image of 0.3%C LCLA sample austempered at 399°C. BF: Bainitic Ferrite, IRA: Islands of Retained Austenite, MA-LB: Martensite or Lower bainite.

Figure.24: SEM images of 0.3%C LCLA sample austempered at 399°C (Etched with 3% Nital) a) upper bainitic sheaf morphology and b) lath shaped morphology of martensite or lower bainite. BF: Bainitic Ferrite, MA-LB: Martensite or Lower bainite.
- the right side) shows typical bainitic sheaf morphology in the SEM image (image on the left side). These sheaves have serrated edges and are arranged parallelly with films of austenite in between them. A high magnification SEM image obtained by etching the same sample with 3% nital is shown in figure 24 a) which-highlights the typical sheaf morphology. Sheaf is made up of group of similar crystallographic oriented bainitic ferrite laths or plates. These plates are called sub units. These subunits are connected with each other and form a sheaf which is a wedge shaped plate in three dimensions [42]. The brown area in the figure 23 shows long parallelly arranged laths with films of austenite between them, which is similar to martensite or lower bainite morphology. These individual lath edges are not serrated. Figure 24 b) shows the high magnification SEM microstructure of the same sample identifying the lath shaped morphology. Figure 23 optical image also shows white regions of blocky austenite and are clearly seen in the SEM image on the left side. There is a clear distinction between sheaf like morphology and the lath like morphology and the sodium metabisulfite gives blue and brown tint effects to these two morphologies.

Sodium metabisulfite gives blue and brown tint effects to martensite and bainite phases respectively. Here the blue color to bainite is justified by the observed classical sheaf morphology of upper bainite. The brown color to the lath shaped morphology can either be martensite or lower bainite. Bainite growth is diffusionless and the trapped carbon diffuses into surrounding austenite. The next bainitic ferrite plate or lath is nucleated from the surrounding high carbon austenite [44]. In low carbon steels, upper bainite formation is predominant and lower bainite forms at the later stages of isothermal transformation from the high carbon austenite region [41]. This is due to the precipitation of carbides inside the laths, which are nucleated from the high carbon austenite region. So the mixture of both upper bainite and lower
bainite can be possible at these austempering temperatures [41]. Martensite can also be formed from the untransformed austenite regions while cooling the sample to the room temperature after austempering treatment. This lath morphology microstructure was very fine to identify and differentiate based on the presence of carbides inside the laths using SEM. An attempt has been made to study this lath morphology under TEM and due to the small sample size it was difficult to find the exact lath morphology regions. Hence the brown phase is identified as martensite or lower bainite. Here onwards the brown colored phase will be referred as martensite or lower bainite (MA-LB). In figure 23, it should be noted that only the islands of retained austenite appear as white color in the optical microscope image. The films of austenite between the sheaves and the laths are not visible in optical microscope. The volume fraction of the white phase calculated using image analysis technique refers only to the islands of retained austenite. The overall retained austenite content is measured using X-ray technique and will be discussed in the following sections. Figure 25 and 26 shows two different areas of the microstructure of the same sample (austempered at 399°C). Three colored regions blue, brown and white are circled and these regions are highlighted in the scanning electron microscopy image. The blue phase is bainitic ferrite and it shows sheaf like morphology. The brown phase is martensite or lower bainite having the lath like morphology and the white phase is islands of retained austenite.

Figure 27 and 28 are few more indented microstructures of the same sample (austempered at 399°C) taken using polarized light. Polarized light was used to improve the contrast of the brown phase. In these two images the blue phase appears to be purple or dark blue in color due to the polarized light. The three regions are circled and the morphologies of these phases are shown in the SEM image on the left side. Similar optical and SEM image comparisons were made using the indentation marker for the samples austempered above and
Figure.25: SEM and optical microscope image of 0.3%C LCLA sample austempered at 399°C. BF: Bainitic Ferrite, IRA: Islands of Retained Austenite, MA-LB: Martensite or Lower bainite.

Figure.26: SEM and optical microscope image of 0.3%C LCLA sample austempered at 399°C. BF: Bainitic Ferrite, IRA: Islands of Retained Austenite, MA-LB: Martensite or Lower bainite.
Figure 27: SEM and Polarized light optical microscope image of 0.3%C LCLA sample austempered at 399°C. BF: Bainitic Ferrite, IRA: Islands of Retained Austenite, MA-LB: Martensite or Lower bainite.

Figure 28: SEM and Polarized light optical microscope image of 0.3%C LCLA sample austempered at 399°C. BF: Bainitic Ferrite, IRA: Islands of Retained Austenite, MA-LB: Martensite or Lower bainite.
below the martensite start temperature. Figure 29 compares the optical and SEM microstructure of the 0.3CLCLA sample austempered at 385°C. This temperature was in the bainitic region and above the martensite start temperature, and similar phases and morphologies were seen in this sample microstructure. The blue bainitic ferrite, brown martensite or lower bainite and white islands of retained austenite with characteristic phase morphologies are seen in the microstructure. Figure 30 microstructure was obtained from the 0.3%C LCLA sample austempered at 260°C, which shows complete tempered martensite microstructure. The 10% sodium metabisulfite imparts brown color to the tempered martensite phase and it is evident from the optical microstructure. The tempered martensite laths are highlighted in SEM image using arrows. From the above observations it is clear that the 10% sodium metabisulfite etchant gives different color contrast to the phases and it is used for further microstructural analysis. Volume fraction analysis of the phases was also carried out using image analysis technique and is -

Figure.29: SEM and optical microscope image of 0.3%C LCLA sample austempered at 385°C. BF: Bainitic Ferrite, IRA: Islands of Retained Austenite, MA-LB: Martensite or Lower bainite.
6.1.2 0.2%C LCLA microstructure.

All the austempered samples were etched with 10% sodium metabisulfite for the tint effect and to obtain optical microscope images. 3% nital was used to obtain microstructure images using SEM. The etching time to get tint effect by using 10% sodium metabisulfite is crucial for good quality optical microscope images. Over etching may cause excessive tinting. But this etching is not sufficient to get better quality SEM images (As seen in figure 23, 25-30). For this purpose samples were etched thoroughly by 3%nital for SEM imaging. Both the SEM and optical images were obtained from the same metallography sample, but they are not from the same area. Figure 31 a) and b) shows the optical and SEM microstructures of 0.2%C LCLA sample austempered at 260°C. The optical microstructure shows completely brown colored phase, which is lath martensite. The SEM microstructures reveal more details about these laths,
inside the laths there are precipitates of carbides and the films of austenite are present between the martensite laths. The martensite lath containing carbide precipitates is called tempered martensite. Since the austempering temperature was below the martensite start temperature, the initial quench, transforms austenite to supersaturated martensite. During the isothermal transformation at 260°C, carbon partitions from supersaturated martensite into austenite by quenching and partitioning mechanism [78]. During the partitioning there is also precipitation of carbides inside the martensite lath and this phenomenon is called auto-tempering.

![Microstructures of 0.2%C LCLA sample austempered at 260°C](image)

(a) Optical, (b) SEM image.


Similar tempered martensite microstructure was found in the sample austempered at 316°C which is shown in figures 32 a) and b). The SEM image in figure 32 b) shows the randomly oriented carbide precipitates, which is characteristics of a typical tempered martensite structure.
Figure 32: Microstructures of 0.2% C LCLA sample austempered at 316°C, a) Optical b) SEM image. TM: Tempered Martensite, RA: Films of Retained Austenite, CP: Carbide Precipitates.

Figure 33: Microstructures of 0.2% C LCLA sample austempered at 371°C, a) Polarized light Optical b) SEM image. BF: Bainitic Ferrite, RA: Films of Retained Austenite, IRA: Islands of Retained Austenite, MA-LB: Martensite or Lower Bainite.
Figure 34: Microstructures of 0.2%C LCLA sample austempered at 399°C, a) Optical b) SEM image.


Figure 33 and 34 shows the microstructures of the samples austempered at 371 and 399°C respectively. These austempering temperatures were at or above the calculated martensite start temperature ($M_s = 371^\circ C$) and in the bainitic region. The polarized light optical microstructure in figure 33 a) shows the presence of bainitic ferrite (regions with dark and light blue colors), martensite or lower bainite (brown colored region) and retained austenite (white colored region). The morphological features of these phases are highlighted in the high magnification SEM image in figure 33 b). Bainitic ferrite shows sheaf like morphology with the serrated edges. The retained austenite is present as films between the bainitic sheaves and it is also present in the form of islands. Only the islands of retained austenite are visible in the optical image as white.
colored phase. Martensite or lower bainite appear as long parallelly arranged laths. Figure 34 a) and b) are the microstructures of the sample austempered at 399°C. Both the optical and SEM images confirm the presence of bainitic ferrite, martensite or lower bainite and retained austenite in the austempered sample. In summary, single step austempering in the bainitic region, which is above the martensite start temperature (371 and 399°C) produced bainitic ferrite microstructure along with martensite or lower bainite and retained austenite. Whereas, austempering below the martensite start temperature (316 and 260°C) resulted in tempered martensite with retained austenite microstructure.

The figure 35 and 36 shows the microstructures of 0.2%C LCLA samples heat treated by two step austempering at temperatures 260-288°C and 316-343°C respectively (as detailed in figure 17(b)). Since these two temperatures were below the calculated martensite start (Mₜ) -

Figure.35: Microstructure of 0.2%C LCLA sample two step austempered at 260-288°C, a) Optical b) SEM image. TM: Tempered Martensite, RA: Films of Retained Austenite, CP: Carbide Precipitates.
Figure 36: Microstructure of 0.2% C LCLA sample two-step austempered at 316-343°C, a) Optical, b) SEM image. TM: Tempered Martensite, RA: Films of Retained Austenite, CP: Carbide Precipitates.

Figure 37: Microstructure of 0.2% C LCLA sample two-step austempered at 371-399°C, a) Polarized light Optical, b) SEM image. BF: Bainitic Ferrite, RA: Films of Retained Austenite, IRA: Islands of Retained Austenite, MA-LB: Martensite or Lower Bainite.
temperature, the microstructures of these samples showed the presence of tempered martensite with films of retained austenite. These microstructures showed the brown color tint effect (figure 35(a) and 36 (a)) when etched with 10% sodium metabisulfite and were similar to the microstructures in figures 31 and 32. Carbides are precipitated inside the martensite laths are clearly seen in the SEM microstructures in figure 35 (b) and 36 (b). Microstructure of the sample two step austempered at 371- 399°C is shown in figure 37 a) and b). Bainitic ferrite appears as light and dark blue color, martensite or lower bainite as brown and austenite appears as off white color in this tint etched polarized light optical image (figure 37 (a)). The corresponding SEM image in 37 (b) shows the morphology of these phases.

From the microstructures in figure 31 to 37 it is evident that the austempering at the above mentioned temperatures results in the microstructures containing tempered martensite, bainitic ferrite, martensite or lower bainite and retained austenite. These are the desired phases to impart high strength to the alloy [30].

6.1.3 0.3%C LCLA microstructures

Austempering heat treatment of 0.3%C LCLA samples were carried out in the temperature range of 260-399°C as detailed in the figure 17(c). Microstructures of the samples austempered at 260 and 288°C, which were below the calculated martensite start ($M_s=364°C$) temperature are shown in figure 38 and 39. Both the optical microstructures figure 38 (a) and 39(a) are completely tempered martensitic with brown color tint effect. SEM images 38 (b) and 39(b) show tempered martensite laths with carbide precipitates and films of retained austenite. These films of austenite did not decompose to cementite during the isothermal hold for 2 hours due to the presence of high silicon content in the steel [32]. Only the martensite laths are auto tempered and the films of austenite are enriched in carbon by quenching and partitioning.
Figure 38: Microstructure of the 0.3% C LCLA sample austempered at 260°C, a) Optical, b) SEM image. TM: Tempered Martensite, RA: Films of Retained Austenite, CP: Carbide Precipitates.

Figure 39: Microstructure of the 0.3% C LCLA sample austempered at 288°C, a) Optical b) SEM image. TM: Tempered Martensite, RA: Films of Retained Austenite, CP: Carbide Precipitates.
- mechanism [78]. The presence of films of austenite and enrichment of austenite with carbon is further confirmed by TEM and X-ray analysis and it is discussed in the following sections. Figure 40 illustrates the microstructure of the sample austempered at 316°C. The polarized light optical image 40 (a)-shows the presence of brown colored martensite or lower bainite and tempered martensite, light and dark purple colored bainitic ferrite (purple color due to the polarized light effect). SEM microstructure figure 40 (b) reveals tempered martensite, bainitic ferrite, films of retained austenite and martensite or lower bainite. From the SEM image, It was able to distinguish tempered martensite from martensite or lower bainite, even though both the phases appear brown in color in the optical micrographs. This austempering temperature was below the martensite start temperature, and the Initial quench from austenitization temperature to the salt bath maintained at 316°C results in certain volume fraction athermal martensite. During the isothermal hold the remainder austenite transforms to bainitic ferrite. The martensite formed during the initial quenching is auto tempered during the isothermal transformation. Martensite or lower bainite phase was also seen in the microstructure which was formed at the later stages of isothermal transformation or during the final air cooling to room temperature [41].

This microstructure in figure 40 is compared with the microstructure of 0.2%C LCLA sample austempered at 316°C in figure 32. The 0.2%C LCLA microstructure doesn’t show presence of any bainitic ferrite phase. Both the alloys have almost same martensite start temperature (Ms: 371 and 364°C) but the bainitic ferrite was not formed in 0.2%C LCLA samples austempered below the martensite start temperature. Carbon plays a major role in determining the temperature range of bainitic ferrite more than the substitutional alloying elements [42]. The TTT diagram in figure 15 shows the larger bainitic temperature range for 0.3%C LCLA alloy compared 0.2%C LCLA alloys (figure 16). The presence of bainitic ferrite
Figure 40: Microstructure of the 0.3%C LCLA sample austempered at 316°C, a) Polarized light optical, b) SEM image. TM: Tempered Martensite, RA: Films of Retained Austenite, CP: Carbide Precipitates, BF: Bainitic Ferrite, MA-LB: Martensite or Lower bainite, IRA: Islands of Retained Austenite.

Figure 41: Microstructure of the 0.3%C LCLA sample austempered at 343°C, a) Polarized light optical, b) SEM image. TM: Tempered Martensite, RA: Films of Retained Austenite, CP: Carbide Precipitates, BF: Bainitic Ferrite, MA-LB: Martensite or Lower bainite, IRA: Islands of Retained Austenite.
Figure 42: Microstructure of the 0.3%C LCLA samples austempered at a) 316°C and b) 343°C.

- below the martensite start temperature indicates that the lower part of the bainitic C curve extends below the martensite start temperature line. This lower part of the bainitic curve can be obtained by extrapolating the curve below the martensite start temperature to know the nucleation time for the corresponding austempering temperatures. The Microstructure of the sample austempered at 343°C in figure 41 (a) and (b) illustrates bainitic ferrite, films of retained austenite and martensite or lower bainite. SEM image 41 (b) shows only the bainitic ferrite, martensite or lower bainite and films of retained austenite phases. Tempered martensite is present in this sample and is shown in figure 42. Figure 42 a) and b) compares the microstructure of samples austempered at 316 and 343°C. Qualitatively it shows that the volume fraction of tempered martensite in the sample austempered at 316°C is more than the sample austempered at 343°C. This is further discussed in the quantitative analysis section. In summary these two sample microstructures contained mixture of phases from both the bainitic ferrite and auto tempered martensitic region. In these samples the initial quench transforms austenite to martensite and the volume fraction of martensite formed can be predicted by the well-known Koistenen-Marburger equation. From the remainder austenite the bainitic ferrite was nucleated at the prior austenite grain boundary and grown into the austenite grain during isothermal hold. Figure 42 a) and b) shows bainitic ferrite formed at the prior austenite grain boundary. In figure 42 a) and b) it should be noted that martensite or lower bainite was formed in the region surrounded by bainitic ferrite indicating that it is formed from the enriched untransformed austenite, during the later stages of isothermal hold.

Microstructures of the samples austempered above the martensite start temperature and in the bainitic region are illustrated in figure 43-45. The optical micrographs 43(a), 44(a) and 45 (a) show blue, brown and white colored tint effects which corresponds to bainitic ferrite, martensite
Figure 43: Microstructure of the 0.3%C LCLA sample austempered at 371°C, a) Polarized light optical b) SEM image. BF: Bainitic Ferrite, RA: Films of Retained Austenite, IRA: Islands of Retained Austenite.

Figure 44: Microstructure of the 0.3%C LCLA sample austempered at 385°C, a) Polarized light optical b) SEM image. BF: Bainitic Ferrite, RA: Films of Retained Austenite, IRA: Islands of Retained Austenite.
Figure 45: Microstructure of the 0.3% C LCLA sample austempered at 399°C, a) Optical b) SEM image. BF: Bainitic Ferrite, RA: Films Retained Austenite, IRA: Islands of Retained Austenite.

- or lower bainite and austenite phases respectively. The morphological features of these phases are clearly seen in the SEM micrographs shown in figure 43(b), 44(b) and 45(b). Bainitic ferrite has sheaf morphology whereas the martensite or lower bainite has lath morphology. Retained austenite is present in the form of films between the sheaves of bainite and laths of martensite or lower bainite. Islands of retained austenite are also identified in these micrographs. Figure 46(a),(b) and (c) shows low magnification SEM microstructures of the samples austempered in the bainite region. These images were taken such that a complete prior austenite grain is seen at the center of the micrograph with a clear grain boundary. It is a well-known fact that the bainite nucleation occurs at grain boundary and the sheaves of bainite grow inside the grain until it is impinged by sheaves which are nucleated at other parts of the same grain. It is evident from the micrographs that the bainitic ferrite covers most part of the grain boundary and the martensite or
- lower bainite formed inside and at the center of the prior austenite grain. These martensite or lower bainite laths are surrounded by bainitic ferrite sheaves indicating that these regions were untransformed austenite at the end of bainitic ferrite growth. These untransformed regions were transformed to either lower bainite at the final stages of isothermal transformation or to martensite at the final air cooling to room temperature.

In summary, austempering heat treatment of the 0.3%C LCLA samples in the temperature range of 260-399°C resulted in three different mixture of phases. Austempering above the martensite start temperature (>=371°C) resulted in the bainitic ferrite and retained
austenite microstructure along with martensite or lower bainite. The samples austempered at 343 and 316°C contained tempered martensite which is auto tempered during isothermal transformation. Along with tempered martensite bainitic ferrite, retained austenite and martensite or lower bainite phases were also observed. Almost completely tempered martensite microstructures were found in the sample austempered below 288°C. The retained austenite was present only in the form of films between the tempered martensite laths.

6.1.4 Transmission electron microscopy

Transmission electron microscopy was carried out to study the microstructure of the austempered samples in detail. It was also used to confirm the presence of films of retained austenite between the sub units and sheaves of bainitic ferrite. Presence of high silicon content (>1.5%) in these steels suppresses austenite decomposition to carbides during the isothermal hold [32]. Selected area diffraction patterns were obtained and indexed to confirm the presence of austenite and other phases. Each diffraction spots were indexed using the equation

\[ d_{hkl}R_{hkl} = \lambda L \]  

\( d_{hkl} \) - lattice spacing of plane (hkl), \( R_{hkl} \) - The distance of the spot from the center beam spot , \( \lambda \) – wavelength of electron beam and \( L \) is the camera length. The product \( \lambda L \) is calibrated using the standard aluminum powder sample of known spacing’s (lattice spacing’s). The calibrated \( \lambda L \) for the operating voltage 200keV is 117.57Å-pixels. The digital micrograph software was used to measure the distance between the center spot and the every other spots and the unit of length measured was in pixels. Using the above equation (11) the \( d_{hkl} \) of each spots were obtained. After obtaining the lattice spacing’s the angle between the each diffraction spots were measured and compared with calculated angle. Finally the symmetry of the diffraction spots was confirmed by calculating the zone axis. Zone axis is a direction in the crystal lattice to which all the
crystallographic planes, which are responsible for diffraction spots are perpendicular. Also the
electron beam direction is parallel to the zone axis. Here an attempt has been made to
differentiate bainitic ferrite and martensite solely on the basis of morphology. This is due to the
fact that the bainite has BCC crystal structure whereas martensite has BCT (body centered
tetragon) crystal structure. The c/a ratio for martensite in 0.2 and 0.3 LCLA steel is nearly equal
to 1.0185 and it’s very close to BCC structure hence the diffraction spots are same for both
bainite and martensite phases. In this investigation, among the 14 austempered samples from 0.2
and 0.3%C LCLA steels, only the six selected samples were chosen for TEM analysis. Samples
were chosen such that they contained all the mixture of phases from the regions above and below
the martensite start temperature. TEM micrographs of 0.2%C LCLA samples austempered at
260-288°C and 371°C, and 0.3%C LCLA samples austempered at 260, 343, 371 and 399°C are
reported here.

Figure 47 shows the TEM micrographs of 0.2%C LCLA samples two step austempered at
260-288°C. The bright field image in figure 47 (a) shows martensite laths which appear bright
with austenite present in between the laths as thin dark films. The dark field image obtained
using the α′(110) martensite reflection is shown in figure 47 (b). These martensite laths do have
carbide precipitates inside them but due to faint diffraction spots of carbides it was not possible
to obtain the dark field image of carbides in this sample. The bright field image in figure 47 (f)
shows clearly the presence of carbide precipitates inside a martensite lath. The dark field image-
- obtained using the γ(200) austenite reflection in figure 47 (c) shows the films of austenite
between the tempered martensite laths. There is no sign of carbides in-between the tempered
martensite laths and the carbides were found to be present inside the laths. This indicates that the
silicon suppresses the decomposition of austenite to carbides. Figure 47(d) and (e) shows the
Figure 47: TEM images of 0.2% C LCLA sample austempered at 260-288°C a) Bright Field image b) Dark field image using \( \alpha'(110) \) martensite reflection c) Dark field image using \( \gamma(200) \) austenite reflection and d) Indexed diffraction pattern of martensite phase.
Figure 47: TEM images of 0.2%C LCLA sample austempered at 260-288°C e): Indexed diffraction pattern of austenite phase, f) Bright field image.

CP: Carbide precipitates.

- indexed diffraction pattern of martensite and austenite phases respectively. Figure 47 (d) selected area diffraction pattern shows only one variant of martensite and the indexing details are reported in table 3 and 4. Table 3 compares the measured d spacing with the calculated d spacing of the diffraction spots. The percentage difference between the measured and calculated d spacing is reported in the table 3. Table 4 reports the measured and calculated angles between the diffracting planes. Table 5 and 6 summarizes the indexing details of the diffraction pattern of the austenite phase. From these tables it is evident that the calculated d spacing and calculated angles between the planes match fairly well with the measured d spacing and angles for both martensite and austenite phases. The zone axis for the martensite phase diffraction spots is [001]
Table 3: Indexing details of diffraction pattern of martensite phase (0.2% C LCLA 260-288°C).

<table>
<thead>
<tr>
<th>Spot</th>
<th>Measured d spacing (Å)</th>
<th>(hkl)</th>
<th>Calculated d spacing (Å)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
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<td>α'(110)</td>
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<td>0.099</td>
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<td>2</td>
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<td>α'(200)</td>
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<td>3</td>
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<td>2.029</td>
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<td>4</td>
<td>1.469</td>
<td>α'(010)</td>
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</table>

Table 4: Indexing details of diffraction pattern of martensite phase (0.2% C LCLA 260-288°C).

<table>
<thead>
<tr>
<th>Angles</th>
<th>Measured angle (°)</th>
<th>hkl</th>
<th>Calculated angle (°)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1∠2 α'</td>
<td>43.25</td>
<td>α'(110)</td>
<td>α'(200)</td>
<td>45</td>
</tr>
<tr>
<td>2∠3 α'</td>
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<td>α'(200)</td>
<td>α'(110)</td>
<td>45</td>
</tr>
<tr>
<td>3∠4 α'</td>
<td>47.51</td>
<td>α'(110)</td>
<td>α'(010)</td>
<td>45</td>
</tr>
<tr>
<td>4∠1 α'</td>
<td>45.15</td>
<td>α'(010)</td>
<td>α'(210)</td>
<td>45</td>
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</tbody>
</table>

Table 5: Indexing details of diffraction pattern of austenite phase (0.2% C LCLA 260-288°C).

<table>
<thead>
<tr>
<th>Spot</th>
<th>Measured d spacing (Å)</th>
<th>(hkl)</th>
<th>Calculated d spacing (Å)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.262</td>
<td>γ(022)</td>
<td>1.272</td>
<td>0.79</td>
</tr>
<tr>
<td>2</td>
<td>2.068</td>
<td>γ(111)</td>
<td>2.078</td>
<td>0.48</td>
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<tr>
<td>3</td>
<td>1.834</td>
<td>γ(200)</td>
<td>1.799</td>
<td>1.95</td>
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<tr>
<td>4</td>
<td>1.108</td>
<td>γ(311)</td>
<td>1.085</td>
<td>2.12</td>
</tr>
</tbody>
</table>
Table 6: Indexing details of diffraction pattern of austenite phase (0.2%C LCLA 260-288°C).

<table>
<thead>
<tr>
<th>Angles</th>
<th>Measured angle (°)</th>
<th>hkl</th>
<th>Calculated angle (°)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 ∠ 2</td>
<td>34.71</td>
<td>γ(022) ∠ γ(111)</td>
<td>35.26</td>
<td>1.56</td>
</tr>
<tr>
<td>2 ∠ 3</td>
<td>55.15</td>
<td>γ(111) ∠ γ(200)</td>
<td>54.74</td>
<td>1.84</td>
</tr>
<tr>
<td>3 ∠ 4</td>
<td>26.14</td>
<td>γ(200) ∠ γ(3 1 1)</td>
<td>25.23</td>
<td>3.61</td>
</tr>
</tbody>
</table>

- and for the austenite phase is [011]. TEM micrographs of 0.2%C LCLA sample austempered at 371°C in figure 48 shows sheaf like upper bainitic ferrite morphology. The bright field image in figure 48 (a) shows sheaves of bainitic ferrite extending from the left end corner of the image to right end corner. The dark black colored films of austenite are present in-between the sheaves. The dark field image obtained using αb(110) bainitic ferrite reflection shows sub-units of bainitic ferrite within these shaves (Figure 48(b)). The first sub unit of a sheaf nucleates at the prior austenite grain boundary and the next sub unit nucleates at the tip of the existing subunit [44]. According the diffusionless growth theory of bainite, the nucleus of bainite is a disassociation of arrays of dislocations in the parent austenite phase and this nucleus grows into a plate or lath of bainite by glide of these dislocations depending on the free energy driving force [54]. The newly developed subunit grows to a limiting size until the parent phase austenite is plastically deformed. This introduces the dislocations in the parent phase and hence making the glide of dislocations difficult [55]. The new plate has to nucleate at the tip of the existing subunit by sympathetic nucleation which gives rise to sheaf like morphology [44]. In figure 48 (b) the sub units in a sheaf have a common crystallographic orientation and the adjacent sheaves are dark and not visible in the dark field image indicating that they have different crystallographic
Figure 48: TEM images of 0.2% C LCLA sample austempered at 371°C a) Bright Field image b) Dark field image using $\alpha_b (110)$ bainitic ferrite reflection c) Dark field image using $\gamma (200)$ austenite reflection and d) Indexed diffraction pattern of bainitic ferrite phase.
- orientation. Only one variant of bainitic ferrite was indexed in the selected area diffraction pattern of bainite phase in figure 48(d). The electron beam direction was parallel to the [001] zone axis. The indexing details are reported in APPENDIX B (Table.B.1). The dark field image of γ(200) austenite reflection shows films of austenite between the sheaves. Very fine films between the subunits are also seen in the TEM micrographs in figure 48(c). The indexed diffraction pattern of austenite phase shows only two faint spots corresponds to γ(111) and γ(200) planes. The zone axis of these two spots is [011]. From the Figures 47 and 48 conclusions can be drawn based on the morphology, that the 0.2% C LCLA sample austempered at 260-288°C microstructure consisted of tempered martensite laths with carbide precipitates inside the laths. These laths are thicker in size and laths didn’t show any subunits and sheaf like morphology. Whereas the sample austempered at 371°C showed sheaf like morphology with subunits. Both
the samples showed the presence of films of austenite between the laths of tempered martensite and sheaves of bainite. Figure 49 illustrates the TEM micrographs of 0.3 LCLA sample austempered at 260°C.

Tempered martensite laths within which cementite precipitates are seen in the bright field image in figure 49 (a). Two variant of martensite are observed in the micrographs which are indexed in the diffraction pattern shown in figure 49(e). Figure 49 (b) and (c) are dark field images obtained using α′(112) and α′(112)II (the subscript II stands for another variant of martensite with different crystallographic orientation) martensite reflections respectively. The electron beam direction was parallel to the two martensite variants having the zone axis [153] and [132]II respectively. Cementite precipitates are identified in figure 49 (d) by obtaining the dark field image using Fe3C (020) cementite reflection.

![TEM images of 0.3%C LCLA sample austempered at 260°C](image)

Figure 49: TEM images of 0.3%C LCLA sample austempered at 260°C a) Bright Field image b) Dark field image using α′(112) martensite reflection
Figure 49: TEM images of 0.3% C LCLA sample austempered at 260°C c) Dark field image using α'(112)_{III} martensite reflection, b) Dark field image using Fe₃C(020) cementite reflection.

Figure 49: TEM images of 0.3% C LCLA sample austempered at 260°C e) Indexed diffraction pattern of martensite phase and f) Indexed diffraction pattern of cementite phase.
The faint Fe₃C (020) was shown in the indexed pattern in figure 49 (f). In the above micrographs no detectable austenite spots were observed in the diffraction patterns. The indexing details of diffraction patterns of both the phases are reported in APPENDIX B (Table.B.2). Figure 50 shows the TEM image of another area from the same sample austempered at 260°C. Bright field image (figure 50 a)) shows the presence of inter lath austenite and martensite laths with two different orientations. Carbide precipitates are not detected due to the faint spots in the diffraction pattern. Figure 50 b) dark field image obtained using the (310) martensite reflection shows martensite laths. Figure 50 c) shows both interlath austenite and another variant of martensite. These two phases are identified in the same dark field image due to the fact the objective aperture covered both spots which are very close to each other. This dark field image was obtained using γ(220) austenite and α'(2T1)II martensite reflections. The indexed diffraction pattern for martensite phase is shown in figure 50 (d). The incident electron beam was parallel to the zone axes of the two martensite variants [135] and [135]II respectively. The indexed austenite diffraction pattern is shown in figure 50 (e) which has zone axis [111] parallel to the incident electron beam. The indexing details are included in the tables in the APPENDIX B (Table.B.3).

From the figures 49 and 50 it is evident that the carbides are precipitated only inside the martensite laths and not between the interlath regions. Austenite is present between the interlaths is confirmed by presence austenite reflections in the selected area diffraction patterns.

Figure 51 illustrates the TEM micrographs of the 0.3%C LCLA sample austempered at 343°C. The bright field image (figure 51(a)) shows bainitic ferrite sub-units with inter-lath austenite. Dark field image (figure 51(b) and (c)) obtained using αb(112) and αb(020) bainitic ferrite reflection show the sub-units of bainitic ferrite. These subunits are lath shaped but their edges are irregular shaped and lengths of these laths are smaller unlike martensite laths. No
Figure 50: TEM images of 0.3% C LCLA sample austempered at 260°C a) Bright Field image b) Dark field image using α’(310) martensite reflection c) Dark field image using γ(220) austenite and α”(2I1) martensite reflection d) Indexed diffraction pattern of martensite phase.
- carbides precipitates are found inside these laths. Other variants of bainitic ferrite laths are also present in the bright field image, but due to the weak diffraction spots intensities it was not possible to obtain the dark field images of these laths. The indexed diffraction pattern for the bainitic ferrite phase is shown in figure 51 (e) which had zone axis of [2 0 1]. The Dark field image obtained using $\gamma(111)$ austenite reflection shows retained austenite present between the bainitic ferrite laths (Figure 51 (d)). There was only one pair of visible austenite phase diffraction spot and is shown in figure 51 (f). Indexing details are reported in APPENDIX B (Table.B.4).

The sample prepared for TEM analysis using twin jet electro-polishing technique resulted in very few good regions which were thin enough for TEM imaging and only the bainitic ferrite with retained austenite was observed in these regions. But the optical and SEM microstructures in figure 41 and figure 42 (b) show the presence of tempered martensite, bainitic ferrite, martensite...
Figure 51: TEM images of 0.3% C LCLA sample austempered at 343°C a) Bright Field image b) Dark field image using $\alpha_b(1 \bar{1} 2)$ bainitic ferrite reflection c) Dark field image using $\alpha_b(0 \bar{2} 0)$ bainitic ferrite reflection d) Dark field image using $\gamma(111)$ austenite reflection.
Figure 51: TEM images of 0.3%C LCLA sample austempered at 343°C e) Indexed diffraction pattern of bainitic ferrite phase f) Indexed diffraction pattern of austenite phase.

- or lower bainite and retained austenite phases in 0.3 LCLA sample austempered at 343°C. Due to the difficulty in finding the exact position in the thin sample using electro-polishing technique, it was not possible to confirm the presence of other phases using TEM imaging technique. It should be noted that the sheaf like morphology observed in both SEM and TEM images for 343°C austempered 0.3 LCLA sample, which confirms the presence of bainitic ferrite phase and it is formed below the martensite start temperature.

The TEM micrographs of the 0.3%C LCLA sample austempered at 371°C are shown in figure 52. Bainitic ferrite sheaf like morphology is observed in the bright field image in figure 52 (a). The dark thin films between the sheaves of bainitic ferrite are believed to be retained austenite. In this sample the austenite phase diffraction spots could not be located in the obtained
Figure 52: TEM images of 0.3%C LCLA sample austempered at 371°C a) Bright Field image b) Dark field image using $\alpha_b (110)$ bainitic ferrite reflection c) Dark field image using $\alpha_{bII} (211)$ bainitic ferrite reflection d) Indexed diffraction pattern of bainitic ferrite phase.
- selected area diffraction. Using $\alpha_b(\overline{1}10)$ and $\alpha_b(211)$ bainitic ferrite reflection dark field images were obtained and are illustrated in figure 52 (b) and (c). These images show two variants of bainitic ferrite subunits connected in a sheaf morphology. In figure 52 c) the bainitic subunits have similar crystallographic orientation within a sheaf but the adjacent sheaf and its subunits have different crystallographic orientation (figure 52(b)). The indexed diffraction pattern for the bainitic phase is shown in figure 52 (d). It shows 2 sets of diffraction spots from bainitic ferrite laths having different crystallographic orientation. The diffraction spots from the first variant of bainitic ferrite has $[\overline{1} 1 0]$ zone axis parallel to the electron beam direction whereas the other variant zone axis is and $[1 \overline{3} 1]_{III}$. Indexing details are reported in APPENDIX B (Table.B.5)

Figure 53 shows TEM images of 0.3%C LCLA sample austempered at 399°C. Bright filed image in figure 53 (a) shows the presence of bainitic ferrite and inter-lath austenite. Figure 53 (b) shows the $\alpha_b(\overline{3}0\overline{1})$ bainitic ferrite reflection dark field image. The image shows single subunit in a sheaf due to the high magnification. The edges of these laths are irregular and serrated and this feature distinguishes them from martensite laths. The low magnification bright field image of another area in the same sample shows (figure 53(f)) typical bainitic ferrite sheaf like morphology. There are two variants of bainitic ferrite are present in the bright field image in figure 53 (a) and only one variant is indexed as shown in figure 53 (d). The zone axis of this variant of bainitic ferrite is $[1 5 \overline{3}]$. Figure 53 (c) dark field image of $\gamma(220)$ austenite reflection shows the thin films of austenite between the bainitic sheaves. There is only one pair of bright spot present in the diffraction pattern (figure 53 (e)) and therefore zone axis was not able to determine for the austenite phase. All the indexing details are reported in APPENDIX B (Table.B.6). A different area from the same sample was again considered for TEM imaging and
Figure 53: TEM images of 0.3% C LCLA sample austempered at 399°C a) Bright Field image b) Dark field image using $\alpha_b(\bar{3}0\bar{1})$ bainitic ferrite reflection c) Dark field image using $\gamma(220)$ austenite reflection, d) Indexed diffraction pattern of bainitic ferrite phase.
Figure 53: TEM images of 0.3% C LCLA sample austempered at 399°C  

- the bright field image of this area in figure 54 (a) shows two variants of bainitic ferrite along with island of retained austenite. Dark field images (figure 54 (b) and (c)) obtained using $\alpha_b(112)$ and $\alpha_{bII}(\bar{1}2\bar{1})$ bainitic ferrite reflection shows two variants of bainitic ferrite sub units. Indexed pattern of the bainitic ferrite phase shown in figure 54 (e) has two zone axes $[1\bar{3}\bar{2}]$ and $[\bar{5}\bar{1}\bar{3}]_{II}$ correspond to each variant, are parallel to the electron beam direction. Island of retained austenite is identified in the dark field image (figure 54 (d)) using $\gamma(111)$ austenite reflection. Due to the faint intensity of diffraction spots from the austenite phase, only one pair of bright austenite diffraction spot is visible in the diffraction pattern shown in figure 54 (f). The indexing details are reported in APPENDIX B (Table B.7)
Figure 54: TEM images of 0.3%C LCLA sample austempered at 399°C a) Bright Field image b) Dark field image using $\alpha_b$(112) bainitic ferrite reflection c) Dark field image using $\alpha_{bII}$(T2T) bainitic ferrite reflection d) Dark field image using $\gamma$(111) austenite reflection.
In summary TEM analysis confirms the presence of mixed microstructures (observed in optical and SEM micrographs) in samples austempered above and below the martensite start temperature. TEM analysis clearly shows the presence of retained austenite in between the laths and bainitic sheaves in all the austempered samples, indicating that the high silicon content suppresses the decomposition of austenite. It also confirms that carbides are precipitated only inside the tempered martensite laths. The presence of martensite or lower bainite phases (brown tint phase) was not confirmed due to the difficulty in locating the exact location in a small (3mm in diameter and 50µm in thickness) TEM sample, using electro-polishing technique used in this investigation. Further research needs to be carried out to fully understand this phase.

Figure 54: TEM images of 0.3% C LCLA sample austempered at 399°C e) Indexed diffraction pattern of bainitic ferrite phase, f) Indexed diffraction pattern of austenite phase.
6.1.5. Quantitative analysis

6.1.5.1 0.2%C LCLA steel

Image pro 6 software was used to quantitatively analyze the volume fractions of phases present in the austempered samples. To measure the volume fraction of the brown colored phase (martensite or lower bainite), all the tint etched microstructures of the austempered samples were photographed using optical microscope camera at 200x magnification. Spatial calibration was done on all the digital image micrographs using the micron marker before measuring the volume fractions of phases. Manual color segmentation was done using either the ‘histogram based’ or ‘color cube based’ option in Count/size tool. Figure 55(a) shows the segmented image of the microstructure of the 0.2%C LCLA sample austempered at 399°C. It shows the segmented red color to the brown phase and figure 55 (b) shows the same microstructure for comparison. Using the ‘count’ option the brown phase area fraction was measured. Microstructures were taken from 8 different areas form the same austempered sample and the above procedure is repeated to measure the area fraction at each location and the average of these values is reported here.

Among all the 7 austempered 0.2%C LCLA steel samples, only samples austempered at 371°C, 399°C and two step austempered at 371-399°C contained martensite or lower bainite (brown colored) phase along with bainitic ferrite and islands of retained austenite (As seen in figure 33,34 and 37). The distinct tint effects on these phases enabled to carry out image analysis to find the phase fractions. Whereas the samples austempered at 316°C, 260°C and two step austempered at 316-343°C, 260-288°C consisted of completely tempered martensitic microstructure along with inter-lath retained austenite (as seen in figures 31, 32, 35 and 36). These microstructures showed completely brown colored phase and inter-lath austenite was visible only in SEM micrographs. Hence X-ray analysis was used to estimate the volume fraction
Figure 55: Image analysis of the microstructure of 0.2\%C LCLA sample austempered at 399°C. 
a) Segmented image to measure the area fraction of the martensite or lower bainite phase,  
b) Same microstructure showing the brown martensite or lower bainite phase for comparison 
(200x).

BF: Bainitic Ferrite, MA-LB: Martensite or Bainite.
- of tempered martensite and inter-lath austenite. Table 7 report the volume fraction of martensite or lower bainite in 0.2% C LCLA austempered samples. Statistical analysis was carried out on the volume fraction data using the student t-test with confidence level set at 95%. The volume fraction of martensite or lower bainite was higher in the sample austempered at 371°C when compared to the sample austempered at 399°C and this increment in volume fraction was statistically significant. Whereas the statistically similar amount of martensite or lower bainite was found in sample two step austempered at 371-399°C when compared to the sample single step austempered at 371°C.

Table 7: Volume fraction of martensite or lower bainite in 0.2% C LCLA austempered samples.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Volume fraction of martensite or lower bainite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>371°C</td>
<td>16.1 ± 2.5</td>
</tr>
<tr>
<td>399°C</td>
<td>9.2 ± 2.1</td>
</tr>
<tr>
<td>371-399°C</td>
<td>13.9 ± 3.8</td>
</tr>
</tbody>
</table>

Optical micrographs show only the white Islands of retained austenite and not the inter-lath austenite. As it can be seen from figure 55 that the white colored austenite phase was not easily detectable due to low magnification (200x) and the color segmentation of this white phase was difficult to carry out using image pro software. Therefore the higher magnification micrographs with magnification of 500x were taken for the volume fraction analysis of islands of retained austenite. Figure 56 (a) shows the segmented image of the microstructure of the 0.2% C LCLA sample austempered at 371°C and 56 (b) shows the white islands of retained austenite.
Figure 56: Image analysis of the microstructure of 0.2%C LCLA sample austempered at 371°C.

(a) Segmented image to measure the area fraction of Islands of austenite, 
(b) Same microstructure showing the white austenite phase for comparison (500x).

BF: Bainitic Ferrite, MA-LB: Martensite or Bainite, IRA: Islands of Retained Austenite.
8 different areas where chosen and photographed from the same sample and using Image pro software the area fractions of islands of retained austenite were obtained. Similar amounts of islands of retained austenite were found in the samples austempered at 371, 399 and 371-399°C as reported in table 8. As pointed out before, the inter-lath austenite cannot be seen in the optical micrographs but SEM micrographs are able to show its presence between the bainitic ferrite sheaves and tempered martensite laths. The inter-lath austenite volume fractions cannot be neglected and therefore X-ray technique was used to obtain the volume fraction of overall austenite in the austempered samples.

Table 8: Volume fraction of islands of retained austenite in 0.2% C LCLA austempered samples.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Volume fraction of islands of retained austenite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>371°C</td>
<td>0.89 ± 0.35</td>
</tr>
<tr>
<td>399°C</td>
<td>1.01 ± 0.45</td>
</tr>
<tr>
<td>371-399°C</td>
<td>0.85 ± 0.18</td>
</tr>
</tbody>
</table>

The austenite volume fraction obtained using X-ray technique includes both the inter-lath and islands of retained austenite. Therefore, volume fraction of islands of retained austenite, which was obtained using the image analysis technique, was subtracted from the overall volume fraction of austenite. Since the samples austempered at 316°C, 260°C and two step austempered at 316-343°C, 260-288°C consisted of two phases tempered martensite and austenite, the overall austenite obtained using X-ray technique is just the inter-lath austenite volume fraction. The tempered martensite volume fraction was obtained by subtracting the austenite fraction from
total volume (100%). Figure 57 shows the X-ray diffraction pattern of samples austempered at 399°C. The pattern shows the presence of both ferrite phase (α) and the γ phase. The pattern was obtained in the 2θ range of 42-46° and 72-92° to get the selected α and γ peaks. All the austempered samples of 0.2%C LCLA steel showed similar diffraction pattern consisting of ferrite and austenite peaks.

Figure 57: X-ray diffraction pattern of 0.2%C LCLA sample austempered at 399°C.
The volume fraction of austenite was calculated using the integrated intensities of (111), and (220) planes of FCC austenite and (110) and (211) planes of BCC ferrite using direct comparison method described in section 3.3. Table 9 reports the volume fraction of austenite and the statistical student t-test analysis carried out on the data concludes that there is no variation in volume fraction of austenite with respect to the austempering temperature.

Table 9: Volume fraction of austenite in 0.2%C LCLA austempered samples.

<table>
<thead>
<tr>
<th>Austempering Temperature</th>
<th>% Volume fraction of Austenite</th>
</tr>
</thead>
<tbody>
<tr>
<td>260°C</td>
<td>4.5 ± 1.7</td>
</tr>
<tr>
<td>316°C</td>
<td>3.1 ± 1.0</td>
</tr>
<tr>
<td>371°C</td>
<td>6.4 ± 1.45</td>
</tr>
<tr>
<td>399°C</td>
<td>8.2 ± 3.2</td>
</tr>
</tbody>
</table>

Table 10 reports the volume fractions of austenite for samples austempered by two step austempering process. Similar levels of volume fractions of austenite were found at respective austempering temperatures when compared with single step austempering samples. There is no statistical significant variation with respect to the two step austempering temperatures.

Table 10: Volume fraction of austenite in 0.2%C LCLA two step austempered samples.

<table>
<thead>
<tr>
<th>Austempering Temperature</th>
<th>% Volume fraction of Austenite</th>
</tr>
</thead>
<tbody>
<tr>
<td>260°C-288°C</td>
<td>4.3 ± 1.2</td>
</tr>
<tr>
<td>316°C-343°C</td>
<td>5.7 ± 0.8</td>
</tr>
<tr>
<td>371°C-399°C</td>
<td>7.0 ± 4.6</td>
</tr>
</tbody>
</table>
From both the tables 9 and 10, it is evident that there is a huge scatter with obtained volume fraction data with X-ray technique. This can be attributed to the fact that the volume fraction of austenite in the 0.2% C LCLA austempered samples was less than 10% and X-ray technique gives poor results when the austenite fractions are low. But the average value close to 5% volume fraction is seen in these austempered samples which are substantially higher than the volume fractions of islands of retained austenite reported in table 8. Using both the image analysis and X-ray analysis data, final volume fractions of all the phases present in the austempered samples were determined under the assumption that the microstructures developed in these samples were homogenous. Bainitic ferrite volume fraction was obtained by subtracting the overall austenite volume fraction and the martensite or lower bainite volume fraction, from the total volume (100%). Inter-lath retained austenite was obtained by subtracting the volume fraction of islands of retained austenite from the overall austenite volume fraction obtained by X-ray technique. Finally tempered martensite was obtained by subtracting overall retained austenite volume fraction from the total volume (100%). The resulting standard deviations of bainitic ferrite and tempered martensite volume fractions were obtained by the square root of sum of squares of standard deviations of the subtracting phases.

Table 11 reports the volume fractions of phases in 0.2% C LCLA single step austempered samples. Statistically similar amount of volume fractions of tempered martensite and retained austenite phases were found in samples austempered at 260 and 316°C. Whereas the bainitic ferrite volume fraction in sample austempered at 399°C was slightly higher but statistical significant than the sample austempered at 371°C. Martensite or lower bainite volume fraction in sample austempered at 399°C was lower than the volume fraction in the sample austempered at 371°C. All the austempered samples austempered above or below the martensite start
temperature contained statistically similar amount of inter-lath retained austenite. Islands of retained austenite found in samples austempered at 371 and 399°C were less than or equal to 1% in volume fraction and no significant difference was observed between these two samples.

Table.11: Volume fractions of phases in 0.2%C LCLA austempered samples.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Volume fraction of bainitic ferrite (V_{ BF})</th>
<th>Volume fraction of martensite or lower bainite (V_{ MA-LB})</th>
<th>Volume fraction of films of retained austenite (V_{ RA})</th>
<th>Volume fraction of Islands of retained austenite (V_{ IRA})</th>
<th>Volume fraction of tempered martensite (V_{ TM})</th>
</tr>
</thead>
<tbody>
<tr>
<td>260°C</td>
<td>-</td>
<td>-</td>
<td>4.5 ± 1.7*</td>
<td>-</td>
<td>95.5 ± 1.7*</td>
</tr>
<tr>
<td>316°C</td>
<td>-</td>
<td>-</td>
<td>3.1 ± 1*</td>
<td>-</td>
<td>96.9 ± 1*</td>
</tr>
<tr>
<td>371°C</td>
<td>77.5 ± 4.1 (75.8)**</td>
<td>16.1 ± 3.8</td>
<td>5.51 ± 1.5*</td>
<td>0.89 ± 0.35</td>
<td>-</td>
</tr>
<tr>
<td>399°C</td>
<td>82.6 ± 3.9 (73.4)**</td>
<td>9.2 ± 2.1</td>
<td>7.19 ± 3.2*</td>
<td>1.01 ± 0.45</td>
<td>-</td>
</tr>
</tbody>
</table>

* Volume fractions of phases obtained by X-ray technique.
** Predicted volume fraction of bainitic ferrite using the Bhadeshia’s diffusionless theory.

Table.12: Volume fractions of phases in 0.2%C LCLA two step austempered samples.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Volume fraction of bainitic ferrite (V_{ BF})</th>
<th>Volume fraction of martensite or lower bainite (V_{ MA-LB})</th>
<th>Volume fraction of films of retained austenite (V_{ RA})</th>
<th>Volume fraction of Islands of retained austenite (V_{ IRA})</th>
<th>Volume fraction of tempered martensite (V_{ TM})</th>
</tr>
</thead>
<tbody>
<tr>
<td>260-288°C</td>
<td>-</td>
<td>-</td>
<td>4.3 ± 1.2*</td>
<td>-</td>
<td>95.7 ± 1.2*</td>
</tr>
<tr>
<td>316-343°C</td>
<td>-</td>
<td>-</td>
<td>5.7 ± 0.8*</td>
<td>-</td>
<td>94.3 ± 0.8*</td>
</tr>
<tr>
<td>371-399°C</td>
<td>79.1 ± 5.2</td>
<td>13.9 ± 2.5</td>
<td>6.15 ± 4.6*</td>
<td>0.85 ± 0.18</td>
<td>-</td>
</tr>
</tbody>
</table>

* Volume fractions of phases obtained X-ray technique.
Figure 58: Variation of volume fractions of different phases with respect to austempering temperature, (a) in 0.2% C LCLA single step austempered samples, (b) in 0.2% C LCLA two step austempered samples.

Table 12 reports the volume fractions of phases in 0.2%C LCLA two step austempered samples. Samples two step austempered at 316-343°C and 260-288°C showed statistically similar amounts of tempered martensite and inter-lath retained austenite. Moreover these volume fractions were again statistically similar to the volume fractions in the samples single step austempered at 260 and 316°C. Also, samples two step austempered at 371-399°C and single step austempered at 371°C showed similar levels of volume fractions of bainitic ferrite, martensite or lower bainite, Islands and inter-lath-austenite. From these data, it can be concluded that the two step austempering yielded similar phases and phase fractions as that of single step austempering. Figure 58 (a) and (b) illustrates the above explained variations of volume fractions of different phases with respect to austempering temperature in 0.2%C LCLA single step and two step austempered samples.

Table 11 also reports the predicted volume fraction of bainite using the diffusionless growth theory of bainite for comparison. Figure 59 shows the calculated phase boundaries for-
0.2%C LCLA steel obtained using the MAP_STEEL_MUCG83 program available in the materials algorithm project (MAP) library of the phase transformations group of the University of Cambridge [103]. This program uses the thermodynamic model developed by Bhadeshia [63] to calculate the $A_{e1}'$ - para-equilibrium carbon concentration in ferrite, $T_o$ curve and $A_{e3}'$- para equilibrium carbon concentration in austenite, using the chemical composition of the steel. The maximum volume fraction of bainite at the respective austempering temperatures can be obtained by drawing a tie line to the $T_o$ and $A_{e1}'$ curves (lever rule) and the volume fraction of bainite is given by equation 6 (Section 2.5). $\bar{x}$ is average carbon concentration of the alloy which is 0.0096 mole fraction (0.2 wt%). For the sample austempered at 399°C the measured volume fraction was higher than the predicted value but for the sample austempered at 371°C reasonable agreement was observed between the measured and the predicted bainitic ferrite volume fraction values (table 11).

6.1.5.2 0.3%C LCLA steel

In 0.3%C LCLA steel, samples austempered in the range of 316-399°C consisted of bainitic ferrite along with martensite or lower bainite and retained austenite. These phases gave distinct tint effects when etched with sodium metabisulfite and therefore image analysis was used for the phase fraction measurement. The samples austempered at 260 and 288°C consisted of completely tempered martensitic microstructure and only the brown tint effect was seen in the optical micrographs (as seen in figure 38 and 39) and hence image analysis was not possible. X-ray technique was used to find the interlath austenite fraction present in between the tempered martensite laths. Micrographs were obtained from the optical microscope at a magnification of 200x, and volume fraction of martensite or lower bainite (brown phase) was measured using
image pro 6 software (as described in the section 6.1.5.1). Figure 60 (a) shows the segmented image with red color to the martensite or lower bainite phase to measure the area fraction. Figure 60(b) is the same microstructure of the 0.3% C LCLA sample austempered at 399°C for comparison. The polarized light optical mode imparted light and dark brown color range to the brown phase and care was taken to select this color range using the “histogram based” or “color cube based” tool.

The SEM and optical images (figures 40, 41 and 42) of the microstructures of the samples austempered at 316 and 343°C, showed the presence of tempered martensite and martensite or lower bainite phase. Both these phases appeared brown under optical microscope when etched with sodium metabisulfite. It should be noted that the volume fractions of the brown phase measured for these two samples (316 and 343°C) includes fractions from both the tempered martensite and martensite or lower bainite phases. Figure 61 (a) shows the segmented image of the microstructure of the sample austempered at 316°C and 61 (b) the same microstructure for comparison and the brown colored phase contains both tempered martensite and martensite or lower bainite phases. Individual tempered martensite laths are not identified in the microstructure in figure 61 (b) due to the low magnification (200x) but it has been identified in the optical (500x) and SEM image in figure 40 in the microstructure section. 8 different areas were analyzed from each austempered samples and the averages of these values are reported in table 13. These values were statistically analyzed using the student t-test with confidence level set at 95%. Statistically similar levels of volume fractions of martensite or lower bainite were found in samples austempered at 385 and 399°C. As the austempering temperature decreases from 385 to 343°C, statistically significant increase in volume fraction of martensite or lower bainite phase was found in samples. Sample austempered at 316°C contained similar levels of-
Figure 60: Image analysis of the microstructure of 0.3% C LCLA sample austempered at 399°C.  
a) Segmented image to measure the area fraction of the martensite or lower bainite phase, b)  
Same microstructure showing the brown martensite or lower bainite phase for comparison.  

BF: Bainitic Ferrite, MA-LB: Martensite or Bainite.
Figure 61: Image analysis of the microstructure of 0.3% C LCLA sample austempered at 316°C. 
a) Segmented image to measure the area fraction of the brown colored phases, b) Same 
 microstructure showing the brown colored phases for comparison.

BF: Bainitic Ferrite, MA-LB: Martensite or Bainite, TM- Tempered Martensite.
Table 13: Volume fraction of martensite or lower bainite in 0.3%C LCLA austempered samples.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Volume fraction of martensite or lower bainite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>316°C</td>
<td>32.3 ± 3.6*</td>
</tr>
<tr>
<td>343°C</td>
<td>30.3 ± 4.1*</td>
</tr>
<tr>
<td>371°C</td>
<td>22.5 ± 4.3</td>
</tr>
<tr>
<td>385°C</td>
<td>18.0 ± 2.8</td>
</tr>
<tr>
<td>399°C</td>
<td>18.8 ± 6.1</td>
</tr>
</tbody>
</table>

* Total volume fraction of tempered martensite and martensite or lower bainite phases.

- volume fractions of brown phase as that of 343°C sample. As pointed out earlier, the measured volume fraction of the brown phase in 316 and 343°C austempered samples include both fractions of tempered martensite and martensite or lower bainite. Hence finding the exact amount of these phases was difficult just using the image analysis technique. To roughly estimate the volume fraction of tempered martensite Koistenen-Marburger equation was used [82]. The initial quench below the martensite start temperature produces certain amount of athermal martensite and untransformed austenite. Koistenen-Marburger equation is

\[
V_M = \exp \left( -\alpha \left( T_{M_s} - T \right) \right)
\]

where \( \alpha \) is the rate parameter and for medium and low carbon steels it is 0.011 [82]. \( T_{M_s} \) is the calculated martensite start temperature. This athermal martensite gets auto tempered during isothermal hold and the untransformed austenite transforms to bainitic ferrite. For the samples austempered at 316 and 343°C, this equation was used to obtain tempered martensite volume.
fraction and subtracted from the total volume fraction of measured using image analysis technique.

As explained in the section 6.1.5.1 volume fractions of islands of retained austenite were measured from the micrographs of 0.3%C LCLA austempered samples taken at a magnification of 500x. Detectable amounts of islands of retained austenite were found in samples austempered at 371, 385 and 399°C. Figure 62 (a) shows the segmented image of the microstructure of the sample austempered at 385°C and 62 (b) shows the same microstructure with white colored islands of retained austenite. Microstructure from the 8 areas from each austempered samples were analyzed using the image pro 6 image analysis software. Table 14 shows the volume fractions of islands of retained austenite in 0.3%C LCLA samples austempered at 371, 385 and 399°C. Based on the statistical analysis, the volume fraction of islands of retained austenite increases as the austempering temperature increases from 371 to 399°C. The samples austempered at 316 and 343°C SEM images in figure 40 and 41 shows few islands of retained austenite but in high magnification (500x) optical micrographs, no detectable amount of islands of retained austenite were seen. In all the austempered samples inter-lath austenite was not visible in the optical microscope and as explained in section 6.1.5.1 X-ray technique was used to measure the volume fraction of inter-lath austenite. Figure 63 shows the X-ray diffraction pattern of sample austempered at 399°C. The pattern shows α and γ peaks. Similar diffraction patterns were obtained for all the 0.3%C LCLA austempered samples. Table 15 shows the volume fractions of overall austenite in the 0.3%C LCLA austempered samples. Less than 8% average volume fraction of overall austenite was found in samples austempered below 316°C and these measured volume fractions were statistical similar. As the austempering temperatures increases from 316 to 371°C significant increase in the measured volume fraction of austenite-
Figure 6.2: Image analysis of the microstructure of 0.3% C LCLA sample austempered at 385°C.

(a) Segmented image to measure the area fraction of Islands of Austenite, b) Same microstructure showing the white austenite phase for comparison.

BF: Bainitic Ferrite, MA-LB: Martensite or Bainite, IRA: Islands of Retained Austenite.
Table 14: Volume fraction of islands of retained austenite in 0.3%C LCLA austempered samples.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Volume fraction of islands of retained austenite (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>371°C</td>
<td>0.7 ± 0.2</td>
</tr>
<tr>
<td>385°C</td>
<td>2.6 ± 0.8</td>
</tr>
<tr>
<td>399°C</td>
<td>4.2 ± 1.0</td>
</tr>
</tbody>
</table>

Table 15: Volume fraction of austenite in 0.3%C LCLA austempered samples

<table>
<thead>
<tr>
<th>Austempering Temperature</th>
<th>% Volume fraction of Austenite</th>
</tr>
</thead>
<tbody>
<tr>
<td>260°C</td>
<td>5.3 ± 2.4</td>
</tr>
<tr>
<td>288°C</td>
<td>5.8 ± 0.9</td>
</tr>
<tr>
<td>316°C</td>
<td>8.8 ± 2.1</td>
</tr>
<tr>
<td>343°C</td>
<td>11.2 ± 2.6</td>
</tr>
<tr>
<td>371°C</td>
<td>12.5 ± 1.7</td>
</tr>
<tr>
<td>385°C</td>
<td>12.3 ± 1.3</td>
</tr>
<tr>
<td>399°C</td>
<td>15.7 ± 3.0</td>
</tr>
</tbody>
</table>

- was found in samples. Statistically similar levels of volume fractions were obtained in the samples austempered above 371°C and the average value of the volume fraction of austenite in these samples were above 12%. Using both the X-ray technique and the image analysis volume-
Figure.63: X-ray diffraction pattern of 0.3\%C LCLA sample austempered at 399\degree C.
fraction data, final fractions of all the phases present in the austempered samples were determined. To determine the final volume fractions of all the phases present, assumption was made that the microstructure developed in these austempered samples were homogenous. In samples austempered at 371, 385 and 399°C, bainitic ferrite volume fraction was obtained by subtracting the volume fraction of martensite or lower bainite phase and overall austenite volume fraction from the total volume (100%). In these 3 samples (371, 385 and 399°C) inter-lath or films of retained austenite volume fraction was determined by subtracting the volume fraction of islands of retained austenite from overall austenite fraction. For samples austempered at 316 and 343°C, the bainitic ferrite fraction was obtained by subtracting the measured volume fraction of the brown phase (which includes fraction of tempered martensite) and the overall austenite fraction, from the total volume (100%). In these samples (316 and 343°C), tempered martensite volume fraction was calculated from the Koistenen –Marburger equation (equation 12) using the calculated Ms temperature and this value was subtracted from the total measured fraction of the brown phase to obtain martensite or lower bainite phase fraction. Since samples austempered at 260 and 288°C contained only the tempered martensite and inter-lath or films of austenite, these phase fractions were determined by X-ray technique. Inter-lath or films of austenite in samples austempered below 343°C was also determined by X-ray technique.

Table 16 reports the determined volume fractions of all the phases present in 0.3%C LCLA austempered samples. Statistical analysis was done on volume fraction data using student t test with confidence level set at 95%. Statically similar fraction of bainitic ferrite was found in samples austempered at 371, 385 and 399°C. As the temperature decreases from 371 to 343°C, bainitic ferrite volume fraction decreases and similar fraction of bainitic ferrite was found in sample austempered at 316°C as compared to 343°C austempered sample.
Table 16: Volume fractions of phases in 0.3% C LCLA austempered samples.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Volume fraction of bainitic ferrite (V_{BF})</th>
<th>Volume fraction of martensite or lower bainite (V_{MA-LB})</th>
<th>Volume fraction of films of retained austenite (V_{RA})</th>
<th>Volume fraction of Islands of retained austenite (V_{IRA})</th>
<th>Volume fraction of tempered martensite (V_{TM})</th>
</tr>
</thead>
<tbody>
<tr>
<td>260°C</td>
<td>-</td>
<td>-</td>
<td>5.3 ± 2.4*</td>
<td>-</td>
<td>94.7 ± 2.4*</td>
</tr>
<tr>
<td>288°C</td>
<td>-</td>
<td>-</td>
<td>5.8 ± 0.9*</td>
<td>-</td>
<td>94.2 ± 0.9*</td>
</tr>
<tr>
<td>316°C</td>
<td>58.9 ± 2.1 (74.9)***</td>
<td>1.1</td>
<td>8.8 ± 2.1*</td>
<td>-</td>
<td>31.2**</td>
</tr>
<tr>
<td>343°C</td>
<td>58.5 ± 4.9 (72.3)***</td>
<td>22.9 ± 4.1</td>
<td>11.2 ± 2.6*</td>
<td>-</td>
<td>7.4**</td>
</tr>
<tr>
<td>371°C</td>
<td>65 ± 4.6 (69.8)***</td>
<td>22.5 ± 4.3</td>
<td>11.8 ± 1.7*</td>
<td>0.7 ± 0.2</td>
<td>-</td>
</tr>
<tr>
<td>385°C</td>
<td>69.7 ± 3.3 (68.5)***</td>
<td>18 ± 2.8</td>
<td>9.7 ± 1.5*</td>
<td>2.6 ± 0.8</td>
<td>-</td>
</tr>
<tr>
<td>399°C</td>
<td>65.5 ± 6.9 (67.2)***</td>
<td>18.8 ± 6.1</td>
<td>11.5 ± 3.2*</td>
<td>4.2 ± 1.0</td>
<td>-</td>
</tr>
</tbody>
</table>

* Volume fractions of phases obtained by X-ray technique.
** Volume fractions of tempered martensite obtained by Koistenen – Marburger equation.
*** Predicted volume fraction of bainitic ferrite using the Bhadeshia’s diffusionless theory.

Statistically similar amount of 18% volume fraction of martensite or lower bainite phase was found in samples austempered at 385 and 399°C, and as the austempering temperature decreases from 385 to 371°C, there is statistically significant increase in martensite or lower bainite phase fraction. Sample austempered at 343°C contained similar level of fraction of martensite or lower bainite phase as compared to sample austempered at 371°C. In this sample (343°C) it should be noted that the fraction of martensite or lower bainite phase was determined from the measured brown phase fraction and by using the Koistenen – Marburger equation as described above. In the sample austempered at 316°C, the determined fraction of martensite – lower bainite phase from
the total measured brown phase and using the Koistnen–Marburger equation, was very less when compared to the fraction determined in the sample austempered at 343°C. Volume fraction of islands of retained austenite increases significantly as the austempering temperature increases from 371 to 399°C. Inter-lath or films of retained austenite volume fractions were low in samples austempered below 316°C and as the temperature increases from 316 to 371°C volume fraction of inter-lath austenite increases. Similar level of fraction of inter-lath austenite was found in samples austempered above 371°C. Koistnen–Marburger equation predicted significant difference in the volume fraction of tempered martensite phase in samples austempered at 343 and 316°C (7.4 and 31.2%). These two volume fraction values were calculated using $M_s=350°C$. Higher volume fraction of 41% tempered martensite is obtained in sample 316°C with the Koistnen–Marburger equation when $M_s=364°C$ was used (actual calculated Ms temperature in figure 15). But the total measured fraction of the brown phase in 316°C sample was 32.3% and the figure 42 a) and b) shows the presence of martensite or lower bainite in both these samples. Hence assumption was made that the $M_s$ temperature of the steel was around 350°C for the sake of calculation. This is justified by the qualitative observation of figure 42 a) and b) where significant difference in fraction of martensite or lower bainite and tempered martensite phases is observed between the samples austempered at 316 and 343°C. Moreover, the experimental $M_s$ temperatures are not determined for these two steels. Statistically similar level of tempered martensite was found in samples austempered at 260 and 288°C (measured using x-ray technique). Figure 64 illustrates the explained variation of volume fractions of different phases with respect to temperature in all the 0.3%C LCLA austempered samples. Table 16 also reports the predicted values of volume fraction of bainitic ferrite using the Bhadeshia’s diffusionless growth model of bainitic ferrite [44, 63] to compare with the measured values.
Figure 64: Variation of volume fractions of different phases with respect to austempering temperature in 0.3% C LCLA austempered samples.


Figure 65: Calculated phase boundaries for 0.3% C LCLA steel.
Figure 65 shows the phase boundaries for 0.3%C LCLA steels calculated using the model [103]. Where, \( A e' \) - para-equilibrium carbon concentration in ferrite, \( T_o \) curve and \( A e' \) - para-equilibrium carbon concentration in austenite. The maximum volume fraction of bainite at each austempering temperature was obtained from equation 6 (section 2.5), which was obtained by drawing a tie line to \( T_o \) and \( A e' \) curve (lever rule). There is a good agreement between the measured and predicted volume fraction of bainitic ferrite for the samples austempered at 371, 385 and 399°C. The measured volume fraction of bainitic ferrite was statistically similar in these 3 samples, but the predicted volume fraction increases as the austempering temperature decreases from 399 to 371°C (table 16). For samples austempered at 316 and 343°C measured volume fraction of 58.9 and 58.5% were obtained whereas the predicted values were 74.9 and 72.3 respectively. This discrepancy is due to the fact that these two temperatures were below the calculated martensite start temperature and the initial quench resulted in martensite (which later gets auto-tempered), and the bainite reaction starts after the athermal martensite formation [84]. The model assumes that there is no other reaction happening during the bainite growth and hence it predicts the higher volume fraction of bainitic ferrite at these temperatures.

6.1.5.3 Carbon content in retained austenite

The austenite carbon content was calculated using the equation (10) by obtaining the austenite lattice parameter \( a_\gamma \) from the austenite diffracted peaks. Table 17, 18 and 19 shows the carbon content of austenite along with ferritic cell size in 0.2%C LCLA single step, two step and 0.3%C LCLA single step austempered samples respectively. Ferritic cell size is a measure of mean free path for dislocation motion. It is evident from the table 17, 18 and 19, that the carbon content in austenite is statistically similar and shows no temperature dependence in all the 0.2 and 0.3%C LCLA samples. But clearly the average carbon concentration in austenite in all the
samples is above 1wt% and confirms that austenite is substantially enriched. The carbon content of austenite at 927°C (at austenitizing temperature) is equal to overall carbon content of the alloy

Table 17: Carbon content in austenite and ferritic cell size in 0.2%C LCLA single step austempered samples

<table>
<thead>
<tr>
<th>Temperature</th>
<th>% of Carbon in Austenite</th>
<th>Ferritic Cell size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>260°C</td>
<td>1.36 ± 0.26</td>
<td>21.1 ± 3.3</td>
</tr>
<tr>
<td>316°C</td>
<td>1.27 ± 0.12</td>
<td>21.4 ± 4.6</td>
</tr>
<tr>
<td>371°C</td>
<td>1.26 ± 0.18</td>
<td>23.1 ± 5.8</td>
</tr>
<tr>
<td>399°C</td>
<td>1.20 ± 0.18</td>
<td>23.7 ± 3.8</td>
</tr>
</tbody>
</table>

Table 18: Carbon content in austenite and ferritic cell size in 0.2%C LCLA two step austempered samples

<table>
<thead>
<tr>
<th>Temperature</th>
<th>% of Carbon in Austenite</th>
<th>Ferritic Cell Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>260-288°C</td>
<td>1.42 ± 0.06</td>
<td>23.4 ± 5.9</td>
</tr>
<tr>
<td>316-343°C</td>
<td>1.23 ± 0.15</td>
<td>21.6 ± 3.0</td>
</tr>
<tr>
<td>371-399°C</td>
<td>1.02 ± 0.09</td>
<td>23.6 ± 3.7</td>
</tr>
</tbody>
</table>

- (i.e., $\bar{X} = 0.2\text{wt}\%$ for 0.2%C LCLA and $\bar{X} = 0.3\text{wt}\%$ for 0.3%C LCLA steel), and is decomposed into bainite, martensite and high carbon austenite ($\approx1\text{wt}\%$). The 1.6wt% and 2 wt% Si present in these two alloys plays major role in enriching austenite with carbon by preventing the precipitation of carbides in austenite [112]. From the TEM images it is shown that $\gamma$ phase is present in the samples and the carbides are precipitated only inside the martensite laths. Above $M_s$ temperature austenite is enriched with carbon by giving out the carbon from the supersaturated bainitic ferrite plates and below $M_s$ temperature the austenite is enriched by the
supersaturated martensite plate (quenching and partitioning) [78]. Both these reactions occur without the partitioning of substitutional atoms and the diffusion of carbon into austenite is -

Table 19: Carbon content in austenite and ferritic cell size in 0.3%C LCLA single step austempered samples

<table>
<thead>
<tr>
<th>Temperature</th>
<th>% of Carbon in Austenite</th>
<th>Ferritic Cell Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>260°C</td>
<td>1.37 ± 0.48</td>
<td>20.4 ± 6.0</td>
</tr>
<tr>
<td>288°C</td>
<td>1.02 ± 0.33</td>
<td>17.6 ± 2.0</td>
</tr>
<tr>
<td>316°C</td>
<td>1.24 ± 0.34</td>
<td>19.8 ± 3.7</td>
</tr>
<tr>
<td>343°C</td>
<td>1.28 ± 0.30</td>
<td>19.7 ± 2.0</td>
</tr>
<tr>
<td>371°C</td>
<td>1.29 ± 0.15</td>
<td>22.4 ± 4.9</td>
</tr>
<tr>
<td>385°C</td>
<td>1.26 ± 0.24</td>
<td>23.9 ± 5.1</td>
</tr>
<tr>
<td>399°C</td>
<td>1.10 ± 0.30</td>
<td>23.8 ± 4.5</td>
</tr>
</tbody>
</table>

- governed by the chemical potential of carbon atoms in both the phases [83]. Table 17, 18 and 19 also reports the Ferritic cell sizes, which show no variations with austempering temperature. The figure 66 illustrates the above explained temperature dependence of the carbon content of austenite in 0.2 and 0.3%C LCLA austempered steels. The average carbon content of austenite in all the samples was higher than 1wt% and is sufficiently enough to stabilize the austenite. Here stabilization of austenite is related to the strain induced transformation to martensite [30]. If the carbon content of austenite is less than the required percent then the transformation to martensite occurs at lower strains during loading leading to low strain hardening and ductility [30]. But the strain induced transformation to martensite during loading was not explored in this investigation.
Figure 67 shows the comparison of volume fractions of 0.2%C LCLA and 0.3%C LCLA austempered samples. The graph shows increase in austenite volume fraction in 0.3%C LCLA-

![Graph showing the comparison of volume fractions of 0.2%C LCLA and 0.3%C LCLA austempered samples.](image)

Figure 66: The carbon content of austenite in 0.2% and 0.3%C LCLA austempered samples.

... samples when compared to 0.2CLCLA steel at all austempering temperatures. Even though the 0.2%C LCLA steel had higher amount of Ni, Mn and Mo (austenite stabilizers) when compared to 0.3%C LCLA, the higher amount of carbon in 0.3%C LCLA steel played a major role in stabilizing the austenite. Retained austenite plays a major role in increasing the strength and toughness of the alloys. TRIP steels contain 7-15% austenite and transform to martensite by strain induced transformation resulting in higher ductility [9]. The TRIP effect is prominent when the retained austenite is stabilized (i.e., enriched with higher carbon content) [30]. 0.3%C
LCLA steels contained austenite volume fraction in the range of 8 to 15% in samples austempered above 343°C, which can be compared to TRIP steels. But the TRIP effect and its influence on mechanical properties are not explored in these two steels.

Figure.67: Comparison of volume fractions of 0.2%C LCLA and 0.3%C LCLA austempered samples.
6.1.6 Lath size measurements

Austempering heat treatment of 0.2 and 0.3%C LCLA steels resulted in very fine microstructures. Phases such as, bainitic ferrite, martensite or lower bainite, tempered martensite and inter-lath austenite are present in the form of laths whereas islands of retained austenite, as the name suggest appear like irregular shaped islands. An attempt has been made to measure the width of laths of these different phases and related to the obtained properties. High magnification SEM images were taken from 5 to 10 different areas from each austempered samples, to measure the width of the laths of all the phases present, using image pro 6 software. All the micrographs were spatial calibrated with the micron marker present on SEM micrographs, using the calibration tool in image pro 6 software. All the widths of laths were measured in the direction perpendicular to their longitudinal axis. Total of 100 lath widths measurements were taken from each phase laths in all the austempered samples and the average value is reported here.

6.1.6.1 0.2%C LCLA Steel

Figure 68 a)-e) illustrates the measurements of width of bainitic ferrite, martensite or lower bainite, tempered martensite, islands of retained austenite and films or inter-lath austenite laths respectively. Table 20 and 21 reports the measured lath sizes of different phases in 0.2%C LCLA single and two step austempered samples respectively. Student t-test was used to determine the statistical significance between these austempered samples lath size data. The samples austempered at 371, 399°C and two step austempered at 371-399°C consisted of bainitic ferrite, martensite or lower bainite and islands of retained austenite phases. Figure 69 a) to c) shows the dependence of width of laths of these 3 phases on austempering temperature. Width of bainitic ferrite laths decreases significantly as the austempering temperature decreases from 399 to 371°C. No statistical significant difference was observed between the widths of bainitic laths
Figure 68: Measurement of width of a) bainitic ferrite laths in 0.3% C LCLA sample austempered at 385°C, b) martensite or lower bainite laths in 0.3% C LCLA sample austempered at 399°C, c) tempered martensite laths in 0.3% C LCLA sample austempered at 260°C, d) islands of retained austenite in 0.3% C LCLA sample austempered at 399°C, e) films of austenite in 0.2% C LCLA sample austempered at 399°C.

Table 20: Lath size measurements of different phases in 0.2% C LCLA austempered samples.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>width of bainitic ferrite lath (L_{BF}) (μm)</th>
<th>width of martensite or lower bainite lath (L_{MA-LB}) (μm)</th>
<th>width of films of retained austenite (L_{RA}) (μm)</th>
<th>width of Islands of retained austenite (L_{IRA}) (μm)</th>
<th>width of tempered martensite lath (L_{TM}) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>260°C</td>
<td>-</td>
<td>-</td>
<td>0.145 ± 0.039</td>
<td>-</td>
<td>1.862 ± 0.771</td>
</tr>
<tr>
<td>316°C</td>
<td>-</td>
<td>-</td>
<td>0.184 ± 0.047</td>
<td>-</td>
<td>1.563 ± 0.734</td>
</tr>
<tr>
<td>371°C</td>
<td>0.307 ± 0.069</td>
<td>0.402 ± 0.126</td>
<td>0.197 ± 0.062</td>
<td>1.456 ± 0.549</td>
<td>-</td>
</tr>
<tr>
<td>399°C</td>
<td>0.382 ± 0.118</td>
<td>0.49 ± 0.133</td>
<td>0.182 ± 0.059</td>
<td>2.202 ± 0.73</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 2.1: Lath size measurements of different phases in 0.2% C LCLA two step austempered samples.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>width of bainitic ferrite lath (L_{BF}) (μm)</th>
<th>width of martensite or lower bainite lath (L_{MA-LB}) (μm)</th>
<th>width of films of retained austenite (L_{RA}) (μm)</th>
<th>width of Islands of retained austenite (L_{IRA}) (μm)</th>
<th>width of tempered martensite lath (L_{TM}) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>260-288°C</td>
<td>-</td>
<td>-</td>
<td>0.151 ± 0.042</td>
<td>-</td>
<td>1.318 ± 0.552</td>
</tr>
<tr>
<td>316-343°C</td>
<td>-</td>
<td>-</td>
<td>0.211 ± 0.058</td>
<td>-</td>
<td>1.357 ± 0.589</td>
</tr>
<tr>
<td>371-399°C</td>
<td>0.323 ± 0.087</td>
<td>0.443 ± 0.135</td>
<td>0.19 ± 0.044</td>
<td>1.886 ± 0.814</td>
<td>-</td>
</tr>
</tbody>
</table>

- in samples austempered at 371 and 371-399°C. Statistical significant difference was found between the measured widths of martensite or lower bainite laths in samples austempered at 371 and 399°C as shown in figure 69 (b). Similarly statistical significant increase in width of martensite or lower bainite was observed in sample two step austempered at 371-399°C when compared to sample single step austempered at 371°C (as shown in figure 69 (b)). Figure 69 c) shows similar dependence of width of islands of retained austenite on austempering temperature as that of martensite or lower bainite lath but the widths of these islands are in the range of 1.5 to 2μm. Figure 69 (d) shows the temperature dependence of width of tempered martensite laths in samples austempered at 260, 316°C, 260-288 and 316-343°C. For single step austempered samples, there is statistical significant decrease in width of tempered martensite lath when the austempering temperature is increases from 260 to 316°C. Whereas for two step austempered samples 260-288 and 316-343°C, no statistical difference was found in the measured width of tempered martensite laths. From the figure 69 (d) it is evident that the single step austempering resulted in slightly thicker but statistically significant tempered martensite laths when compared
Figure 69: Dependence of width of a) bainitic ferrite lath, b) martensite or lower bainite lath, c) islands of retained austenite, d) tempered martensite lath on austempering temperature, in 0.2% C LCLA single step and two step austempered samples.
- to two step austempered samples. Films of retained austenite were present in all the 7 austempered samples. For the single step austempered samples 316, 371 and 399°C, measured widths of films of austenite showed no statistical significant difference and when the temperature decreases from 316 to 260°C, the width of the films of austenite decreases as shown in figure 69 (e). For the two step austempered samples as the initial quench temperature decreases from 371 to 316°C width of films of austenite increases statistically and when the temperature decreases from 316 to 260°C the width of films of austenite decreases (as shown in figure 69 (e)).

### 6.1.6.2 0.3%C LCLA Steel

Table 22 reports the width of all the laths of different phases present in 0.3 C LCLA samples. Statistical analysis was carried out to determine the significant difference between two measured sets. Figure 70 a) to e) shows the change in size of lath of different phase with respect to temperature. Bainitic ferrite and martensite or lower bainite phases were found in samples austempered in the range of 316 to 399°C.
Table.22: Lath size measurements of different phases in 0.3%C LCLA austempered samples.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>width of bainitic ferrite lath (L_{BF}) (μm)</th>
<th>width of martensite or lower bainite lath (L_{MA-LB}) (μm)</th>
<th>width of films of retained austenite (L_{RA}) (μm)</th>
<th>width of Islands of retained austenite (L_{IRA}) (μm)</th>
<th>width of tempered martensite lath (L_{TM}) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>260°C</td>
<td>-</td>
<td>-</td>
<td>0.196 ± 0.056</td>
<td>-</td>
<td>1.121 ± 0.559</td>
</tr>
<tr>
<td>288°C</td>
<td>-</td>
<td>-</td>
<td>0.185 ± 0.051</td>
<td>-</td>
<td>0.906 ± 0.278</td>
</tr>
<tr>
<td>316°C</td>
<td>0.325 ± 0.077</td>
<td>0.412 ± 0.123</td>
<td>0.194 ± 0.045</td>
<td>-</td>
<td>2.109 ± 1.111</td>
</tr>
<tr>
<td>343°C</td>
<td>0.332 ± 0.089</td>
<td>0.446 ± 0.129</td>
<td>0.16 ± 0.037</td>
<td>-</td>
<td>1.461 ± 0.86</td>
</tr>
<tr>
<td>371°C</td>
<td>0.296 ± 0.075</td>
<td>0.357 ± 0.093</td>
<td>0.183 ± 0.051</td>
<td>1.2 ± 0.465</td>
<td>-</td>
</tr>
<tr>
<td>385°C</td>
<td>0.271 ± 0.076</td>
<td>0.339 ± 0.099</td>
<td>0.188 ± 0.052</td>
<td>1.631 ± 0.812</td>
<td>-</td>
</tr>
<tr>
<td>399°C</td>
<td>0.298 ± 0.081</td>
<td>0.329 ± 0.085</td>
<td>0.195 ± 0.062</td>
<td>2.131 ± 1.018</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure.70: Dependence of width of a) bainitic ferrite lath , b) martensite or lower bainite lath, on austempering temperature, in 0.3%C LCLA austempered samples.
Figure 70: Dependence of width of (c) islands of retained austenite, (d) tempered martensite lath, and (e) films of retained austenite on austempering temperature, in 0.3% C LCLA austempered samples.
Figure 70 (a) and (b) shows the variation of width of lath of these two phases with respect to temperature. There is no significant difference in between measured width of bainitic ferrite in the samples austempered at 385 and 399°C. The width of bainitic ferrite increases significantly as the austempering temperature decreases from 385 to 343°C and then it shows no statistical significant difference in width as the temperature further decreases to 316°C (Figure 70(a)) . Statistically similar measured width of martensite or lower bainite laths were obtained in samples austempered at 371,385 and 399°C. Increase in width of martensite or lower bainite lath was observed as the temperature decreases from 371 to 343°C and then there is no statistically significant change in the width of lath as the temperature further decreases to 316°C (Figure 70 (b)). Detectable amount of islands of retained austenite were found in the samples austempered in the range of 371 to 399°C. Figure 70 c) shows the width of islands of retained austenite statistically significantly decreases as the austempering temperature decreases from 399 to 371°C. Tempered martensite phase was found in samples austempered below 343°C. As the austempering temperature decreases from 343 to 316°C the width of tempered martensite lath increases significantly, further decrease in temperature to 288°C results in decrease in width of lath and finally it increases in its width as the temperature is reduced to 260°C. These variations in width of tempered martensite laths are statically significant. From the figure 70 (d), it is evident that the width of laths in samples austempered at 316 and 343°C are thicker when compared to the laths present in samples austempered at 260 and 288°C. Films of retained austenite were present in all the 0.3%C LCLA austempered samples. Statistically similar measured width of films of austenite were obtained in all the austempered samples except for the sample austempered at 343°C, which had slightly less but statistically significant width of films of austenite when compared to other austempered samples (Figure.70(e)).
6.2 Structure-property relationship

6.2.1 0.2%C LCLA steel

Table 23 reports the mechanical properties of 0.2%C LCLA as-cast and austempered samples. Student t test was used for the statistical analysis of the mechanical property data. Austempered samples have higher hardness, yield strength, ultimate tensile strength and fracture toughness when compared to the as-cast sample. Hardness of the samples austempered at 371 and 399°C are statistically similar and as the austempering temperature decreases below 371°C, the hardness of the samples increases. As the austempering temperature decreases from 399 to 260°C, yield strength of the samples increases.

Table 23: Mechanical properties of 0.2%C LCLA steel single step austempered samples.

<table>
<thead>
<tr>
<th>Quench Temperature</th>
<th>Hardness (HRC)</th>
<th>Yield Strength (MPa)</th>
<th>Ultimate Tensile Strength (MPa)</th>
<th>% Elongation</th>
<th>Strain Hardening Exponent (n)</th>
<th>Fracture Toughness (MPa√m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Cast</td>
<td>34.3 ± 1.8</td>
<td>478 ± 5</td>
<td>724 ± 2</td>
<td>10.5 ± 0.1</td>
<td>0.16 ± 0.01</td>
<td>54 ± 4</td>
</tr>
<tr>
<td>260°C</td>
<td>42.4 ± 1.3</td>
<td>1199 ± 1</td>
<td>1392 ± 10</td>
<td>3.8 ± 0.1</td>
<td>0.12 ± 0.01</td>
<td>114 ± 2</td>
</tr>
<tr>
<td>316°C</td>
<td>40.6 ± 0.8</td>
<td>1180 ± 7</td>
<td>1358 ± 18</td>
<td>7.1 ± 0.5</td>
<td>0.11 ± 0.004</td>
<td>109 ± 6</td>
</tr>
<tr>
<td>371°C</td>
<td>37.4 ± 1.2</td>
<td>1052 ± 6</td>
<td>1329 ± 2</td>
<td>8.2 ± 0.1</td>
<td>0.13 ± 0.004</td>
<td>77 ± 9</td>
</tr>
<tr>
<td>399°C</td>
<td>37.7 ± 0.5</td>
<td>857 ± 20</td>
<td>1293 ± 1</td>
<td>8.4 ± 0.1</td>
<td>0.20 ± 0.001</td>
<td>54 ± 9</td>
</tr>
</tbody>
</table>

High level of increase in yield strength (857 to 1052 MPa) was observed between the samples austempered at 399 and 371°C whereas slight but statistically significant increase in yield strength (1180 to 1199 MPa) was observed between the samples austempered at 316 and
260°C. Ultimate tensile strength of the samples increases as the austempering temperature decreases up to 316°C and statistically similar ultimate tensile strength was observed between the samples austempered at 316 and 260°C. Ductility (%elongation) of the samples decreases from 8.4 to 3.8% as the austempering temperature decreases from 399 to 260°C. Strain hardening exponent of the samples austempered at 371, 316 and 260°C are statistically similar but the sample austempered at 399°C showed higher strain hardening exponent when compared to the other austempered samples. Statistically constant fracture toughness was observed between the samples austempered at 260 and 316°C and as the austempering temperature increases above 316°C, the fracture toughness of the austempered samples decreases. It should be noted that at lower austempering temperatures the ductility is low, whereas the fracture toughness is high. In conventional alloys, when the ductility is low, fracture toughness is also less and strength is higher. This steel on the other hand has the combination of high strength and fracture toughness.

Table 24 reports the mechanical properties of 0.2%C LCLA steel two step austempered samples. Statistical analysis implies that there is significant increase in hardness as the two step austempering temperature (initial quench temperature) decreases from 399 to 260°C. Yield strength increases as the two step austempering temperature (initial quench temperature) decreases from 371 and 316°C and as the temperature decreases to 260°C, yield strength is statistically similar. No statistically significant difference was observed between the ultimate tensile strength of samples austempered at 260-288 and 316-343°C. As the temperature increases above 371°C, ultimate tensile strength decreases. Ductility (% elongation) in all the samples was less than 5% and statistically similar values were observed between samples austempered at 260-288 and 316-343°C. Strain hardening exponent of all the two step austempered samples were statistically similar.
Table 24: Mechanical properties of 0.2%C LCLA steel two step austempered samples.

<table>
<thead>
<tr>
<th>Quench Temperature</th>
<th>Hardness (HRC)</th>
<th>Yield Strength (MPa)</th>
<th>Ultimate Tensile Strength (MPa)</th>
<th>% Elongation</th>
<th>Strain Hardening Exponent (n)</th>
<th>Fracture Toughness (MPa√m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Cast</td>
<td>34.3 ± 1.8</td>
<td>478 ± 5</td>
<td>724 ± 2</td>
<td>10.5 ± 0.1</td>
<td>0.16 ± 0.01</td>
<td>54 ± 4</td>
</tr>
<tr>
<td>260°C-288°C</td>
<td>42.6 ± 0.5</td>
<td>1225 ± 30</td>
<td>1402 ± 20</td>
<td>3.4 ± 0.1</td>
<td>0.11 ± 0.01</td>
<td>141 ± 7</td>
</tr>
<tr>
<td>316°C-343°C</td>
<td>40.5 ± 0.8</td>
<td>1221 ± 16</td>
<td>1392 ± 14</td>
<td>3.5 ± 0.1</td>
<td>0.11 ± 0.003</td>
<td>127 ± 1</td>
</tr>
<tr>
<td>371°C-399°C</td>
<td>37 ± 0.8</td>
<td>1068 ± 8</td>
<td>1276 ± 2</td>
<td>4.1 ± 0.3</td>
<td>0.12 ± 0.01</td>
<td>97 ± 0.4</td>
</tr>
</tbody>
</table>

Fracture toughness increases from 97 to 141 MPa√m as the two step austempering temperature decreases from 371-260°C. Mechanical properties of the two step austempered samples are compared with the properties of corresponding single step austempered samples. From table 23 and 24, it is evident that the two step austempering of 0.2%C LCLA steel did not result in improved hardness, yield strength and ultimate tensile strength. Ductility of two step austempered samples are lower than the single step austempered samples, except the samples austempered at 260 and 260-288°C showed similar levels of %elongation. Only the fracture toughness values of the two step austempered samples (260-288°C, 316-343°C and 371°C-399°C) are significantly higher than the corresponding single step austempered samples (260°C, 316°C and 371°C). It should be noted that in 0.2%C LCLA steel, samples single and two step austempered at and below 316°C resulted in higher mechanical properties than the samples austempered above 316°C. This is due to the fact that the calculated Ms temperature for 0.2%C LCLA steel is equal to 371°C and austempering at and below 316°C resulted in tempered martensitic microstructure.
Tempered martensite is a very hard phase due to the higher dislocation density within each lath, and along with fine inter-lath austenite it imparts higher strength to the alloy with lower ductility. Samples austempered above 316°C have bainitic ferrite microstructure and the bainitic sheaves contain fine subunits of bainitic ferrite along with inter-lath austenite. The finer Bainitic ferrite laths contribute higher strength to the alloy but not as high as tempered martensite microstructure. An attempt has been made to relate the phase fractions of different phases and their lath sizes to the obtained mechanical properties. Figure 71 a) and b) shows the effect of volume fractions of different phases on the yield strength of 0.2%C LCLA single and two step austempered samples respectively. Yield strength increases from 857 to 1052 MPa as the austempering temperature decreases from 399 to 371°C. This is due to the fact that the volume fraction of martensite or lower bainite increases and the volume fraction of bainitic ferrite decreases in the sample austempered at 371°C when compared to sample austempered at 399°C. Both the samples contained similar volume fraction of films of austenite and islands of retained austenite as shown in figure 71 a). Conclusion can be made that the increase in strength between these two samples is due to the variation in phase fractions of bainitic ferrite and martensite or lower bainite. Moreover, slight but statistically significant decrease in width of bainitic ferrite lath, martensite or lower bainite lath and islands of retained austenite as the austempering temperature decreases from 399 to 371°C. This is illustrated in figure 72 a), b) and c) which shows the effect of width of a) bainitic ferrite lath, b) martensite or lower bainite lath, c) islands of retained austenite on the yield strength of 0.2%C LCLA single step (371 and 399°C) and two step (371-399°C) austempered samples. Similar amounts of volume fractions of bainitic ferrite, martensite or lower bainite, islands and films of retained austenite phases were present in samples austempered at
Figure 7.1: Effect of volume fraction of different phases on yield strength a) single step austempering b) two step austempering of 0.2%C LCLA steel. BF: Bainitic Ferrite, TM: Tempered Martensite, MA-LB: Martensite or lower bainite, IRA: Islands of Retained Austenite, RA: Films of Retained Austenite.
Figure 7.2: Effect of width of a) bainitic ferrite lath, b) martensite or lower bainite lath, c) islands of retained austenite, d) tempered martensite lath on the yield strength of 0.2% C LCLA single and two step austempered samples.
Figure 72: Effect of width of e) films of retained austenite on the yield strength of 0.2%C LCLA single and two step austempered samples.

-371 and 371-399°C. Hence these two samples had statistically similar yield strength values (1052 and 1068 MPa in 371 and 371-399°C respectively) as shown in figure 71 a) and b). Statistically similar bainitic ferrite lath widths, but slightly increased width of martensite or lower bainite and islands of retained austenite laths were found in sample austempered at 371-399°C when compared to the 371°C sample (figure 72 a),b) and c)). As shown in figure 72 b) and c), these slight statistical significant variations (increase) in lath widths of martensite or lower bainite and islands of retained austenite did not affect the yield strength of the sample austempered at 371-399°C when compared to 371°C sample. All the 4 samples single step austempered at 316, 260°C and two step austempered samples 260-288°C, 316-343°C consisted of nearly 95% volume fraction of tempered martensite along with 5% of films of retained austenite. These similar phase fractions in two step austempered samples resulted in statistically similar yield strengths whereas slight but significant increases in yield strength (1180-1199MPa) is observed in the single step austempered samples, which is shown in figure 71 a) and b).
Figure 72 d) shows the effect of width of tempered martensite lath on the yield strength of 0.2%C LCLA single and two step austempered samples. No variations in lath sizes of the two step austempered samples (260-288°C, 316-343°C) were observed and this can be attributed to the same levels of yield strength observed in these samples. Whereas slight increase in the lath sizes were found between the single step austempered (316°C and 260°C) samples, which resulted in small increase in the yield strength. Figure 72 e) shows the effect of films of retained austenite on yield strength. Since the samples austempered at 371, 399°C and 371-399°C had statistically similar width of films (figure 69(e)) and volume fractions of austenite, the variations in yield strength can be hypothesized due to the presence of other phases in these austempered samples. But the decrease in width of films of austenite between the single step austempered samples 316 and 260 (figure 69(e)) resulted in small significant increase in yield strength (1180 to 1199MPa). The decrease in width of films of austenite between the two step austempered samples 316-343°C and 260-288°C (figure 69(e)), had no effect on yield strength. It should be noted that all the films of austenite are sufficiently enriched with carbon and stabilized as explained in the section 6.1.5.1. Even though the volume fraction of austenite is low in all the 0.2%C LCLA austempered samples, the strain induced transformation to martensite cannot be ruled out during the loading. Further investigation needs to be carried out to confirm this and verify the contribution of films of retained austenite on properties.

The volume fraction of different phases present in single step austempered samples has similar effect on fracture toughness as compared to the effect on yield strength (71 (a) and 73(a)). The increase in fracture toughness in sample austempered at 371°C (77 MPa√m) when compared to the sample austempered at 399°C (54 MPa√m), is due to the difference in volume fractions of martensite or lower bainite and bainitic ferrite phases, as illustrated in figure 73 (a).
Figure 73: Effect of volume fraction of different phases on fracture toughness a) single step austempering b) two step austempering of 0.2%C LCLA steel. BF: Bainitic Ferrite, TM: Tempered Martensite, MA-LB: Martensite or lower bainite, IRA: Islands of Retained Austenite, RA: Films of Retained Austenite.
Figure 74: Effect of width of a) bainitic ferrite lath, b) martensite or lower bainite lath, c) islands of retained austenite, d) tempered martensite lath on the fracture toughness of 0.2%C LCLA single and two step austempered samples.
Figure 74: Effect of width of e) films of retained austenite on the fracture toughness of 0.2%C LCLA single and two step austempered samples.

Figure 74 (a), (b) and (c) shows the effect of width of bainitic ferrite, martensite or lower bainite and islands of retained austenite on fracture toughness. As the width of the laths of these phases decreases the fracture toughness increases. Sample two step austempered at 371-399°C resulted in higher fracture toughness (97MPa√m) when compared to single step 371°C sample (77 MPa√m), even though the similar phases and phase fractions are found in these two samples(figure 73 (a) and (b)). Figure 74 a) shows statistically similar width of bainitic ferrite but figure 74 (b) and (c) shows the slight increase in width of martensite or lower bainite and islands of retained austenite of the sample austempered at 371-399°C when compared to single step 371°C sample. The slight increase in the lath width of these phases cannot be solely responsible for the increase in fracture toughness, since these two phases had very less volume fractions (MA-LB – 13% and IRA – 0.85%). Moreover combined effect of phase fractions and
lath sizes of bainitic ferrite, films of retained austenite and with these above mentioned two phases (MA-LB and IRA) are responsible for the increase in fracture toughness. The samples single step austempered at 316 and 260°C showed similar levels of fracture toughness (109 and 114 respectively MPa√m). As shown in figure 73 (a) these two samples had similar volume fractions of tempered martensite and films of retained austenite. Figure 74 (d) shows the increase in lath size of tempered martensite as the temperature decreases from 316 to 260°C which resulted in similar level of fracture toughness. Statistically significant increase in fracture toughness is observed between the sample austempered at 316-343°C and 260-288°C (127 to 141 MPa√m), even though they had statistically similar lath sizes (as shown in figure 74 (d)). This increase in fracture toughness is attributed to the decrease in width of films of retained austenite, along with combined effect of tough tempered martensite laths, when the two step temperature is reduced from 316 to 260°C, which is illustrated in figure 74 (e). It is evident from the figure 74 (d) and figure 69 (d) that the lath sizes of tempered martensite in two step austempered samples are finer than single step austempered samples, which can be a reason for higher fracture toughness observed in the samples two step austempered at 316-343°C and 260-288°C.

Figure 75 shows the fractographs of the fractured surfaces of compact specimen (CT) of single step austempered samples. Fractured surface shows both quasi-cleavage fracture and dimple ductile fracture. Cleavage fracture is a brittle form of fracture and dimples or micro-void indicates ductile fracture. The sample austempered at 260°C shows high degree of dimpled fracture with very little quasi-cleavage fracture explaining the high fracture toughness. As the austempering temperature increases the quasi-cleavage fracture increases and the sample austempered at 399°C shows high degree of quasi-cleavage fracture and very little dimpled fracture resulting in lower fracture toughness.
Figure 75: Fractographs obtained from the fractured surface of Compact Tension (CT) specimen 0.2%C LCLA samples single step austempered at a) 260°C, b) 316°C, c) 371°C, d) 399°C respectively. QC, QF - quasi cleavage fracture, DF - Dimpled ductile fracture.
Figure 76: Fractographs obtained from the fractured surface of Compact Tension (CT) specimen 0.2%C LCLA samples two step austempered at a) 260-288°C, b) 316-343°C, and 371-399°C respectively. QF - quasi cleavage fracture, DF - Dimpled ductile fracture

From figure 76 it is evident that only the fractured surface of sample two step austempered at 371-399°C showed the presence of quasi cleavage and dimpled ductile fracture,
and as the result (table 24) show this sample had the lowest fracture toughness among the two step austempered samples. The other two samples showed only dimpled ductile type of fracture. From the microstructures and the properties obtained by austempering process in 0.2%C LCLA, it can be concluded that this steel had combination of high strength and fracture toughness. The single step austempering yielded tensile strength in the range of 1293-1392MPa and the fracture toughness in the range of 54-114MPa√m and Two step austempering resulted in tensile strength in the range of 1276-1402 MPa and fracture toughness in the range of 97-141MPa√m. These properties are higher than first generation high strength steels and the fracture toughness of these steels can be compared with maraging steels and fall into the category of third generation advanced high strength steels.

6.2.2 0.3%C LCLA steel

Mechanical properties of the 0.3%C LCLA steel austempered samples are reported in table 25. Highest Hardness is obtained in the samples austempered at 260 and 288°C and these two values are statistically similar. As the temperature increases from 288 to 385°C, hardness of the austempered samples decreases. Sample austempered at 399°C showed slightly higher hardness when compared to the sample austempered at 385°C. Yield strength of the samples significantly increases from 1038 to 1178 MPa as the austempering temperature decreases from 399 to 371°C. There is a sudden increment in yield strength from 1178 MPa to 1344 MPa as the temperature is further decreases to 343°C. Same level of yield strength is observed in the sample austempered at 316 as compared to the sample austempered at 343°C. Highest yield strength of 1411 MPa is observed in sample austempered at 288°C and austempering below 288°C resulted in statistically similar yield strength. Ultimate tensile strength increases as the austempering temperature decreases from 399 to 385°C and statistically similar ultimate tensile strength was
- observed in sample austempered at 371°C as compared to 385°C. The ultimate strength increases from 1302 MPa to 1337 MPa as the temperature is decreases from 399 to 371°C. This increment is significant but smaller when compared to the increment observed when the temperature decreases from 371 to 343°C (i.e., 1337MPa to 1515 MPa). As the temperature decreases below 343°C, ultimate tensile strength increases and it reaches the maximum value of 1658 MPa at the temperature of 288°C. Below 288°C, as the temperature decreases to 260°C, the ultimate strength decreases from 1658MPa to 1613 MPa. Ductility (% elongation ) of the samples austempered below 288°C showed very low values and the highest % elongation of
9.2% was observed in sample austempered at 399°C. Statistically similar level of ductility is observed between the 399 and 385 austempered samples and as the temperature is reduced to 371 the ductility decreases. Moderate ductility of 7.7 and 5.9 % along with very high strength is observed in samples austempered at 343 and 316°C respectively. Strain hardening exponent is statistically similar in all the austempered samples except for the sample austempered at 343°C, which showed the lowest strain hardening exponent of 0.09. Fracture toughness increases from 80 to 139 MPa√m as the austempering temperature decreases from 399 to 343°C and as the temperature decreases from 343 to 288°C statistically similar level of fracture toughness is observed in these samples. Fracture toughness of the sample austempered at 260°C is lower than that of the sample austempered at 288°C, as reported in table 25.

Sample austempered below 343°C showed superior mechanical properties when compared to the sample austempered above 371°C. This is due to the difference in microstructures obtained in these samples (Similar to 0.2%C LCLA steel). The calculated Ms temperature for this steel is 364°C and austempering above 371°C resulted in predominantly bainitic ferrite phase along with martensite or lower bainite and films and islands of retained austenite phases. Whereas mixed microstructure of bainitic ferrite, tempered martensite and martensite or lower bainite phases along with austenite were found in samples austempered at 343 and 316°C (as discussed in the microstructure section). Below 288°C almost complete tempered martensitic microstructure along with very low amount of films of retained austenite. The mixed microstructure and tempered martensite microstructure imparted superior mechanical properties to the steel when compared to bainitic microstructure. The difference in mechanical properties of the samples austempered between 288°C to 343°C is very low. They had very high yield strength in the range of 1344 to 1411 MPa and fracture toughness in the range of 133 -139
MPa√m and good ductility in the range of 5.8 to 7.7% with very low strain hardening exponent. These combinations of very high properties can be obtained by austempering at any temperature in the temperature range of 288°C to 343°C. This indicates that the current austempering (or quench and partitioning) process below the \( M_s \) temperature is very robust to variations in thermal processing. Thus, this steel has a high chance of commercialization by applying this process.

The observed mechanical properties are related to the measured volume fractions and lath sizes of different phases present in the 0.3%C LCLA steel. Figure 77 illustrates the effect of different phases present in the austempered samples. Samples austempered at 399 and 371°C consisted of statistically similar volume fractions of bainitic ferrite, martensite or lower bainite and films of retained austenite phases. Whereas volume fraction of islands of retained austenite decreases significantly as the temperature decreases from 399 to 385°C (figure 77). Also the lath sizes of islands of retained austenite decreases statistically as the austempering temperature decreases, which is shown in figure 78 (c). But the lath sizes of bainitic ferrite and martensite or lower bainite phases are similar in these two samples as shown in figure 78 (a) and (b). This variation in volume fraction of phases and their lath sizes resulted in the increase in the yield strength in the sample austempered at 385°C (i.e., 1038 to 1113MPa). It has been shown that the presence of islands of retained austenite in significant amount is detrimental to mechanical properties [32]. These islands are not sufficiently enriched in carbon compared to films of retained austenite. Hence they are not stable and transform to strain induced transformation to martensite at low levels of strains during tensile loading, which results in poor mechanical properties [30]. Further decrease in temperature from 385 to 371°C results in increase in yield strength (1113 to 1178MPa) and this can be attributed to the increase in volume fraction of martensite or lower bainite and decrease in volume fraction of bainitic ferrite and islands of -
Figure 77: Effect of volume fraction of different phases on yield strength of 0.3%C LCLA steel.


- retained austenite phases in the 371°C austempered sample compared to sample austempered at 385°C (figure 77). From figure 78 (a) and (b), Bainitic ferrite width increases slightly whereas the statistically similar lath size of martensite or lower bainite is present in the sample austempered at 371°C compared to 385°C. Moreover, statistically significant decrease in lath size of islands of retained austenite is observed as the temperature decreases from 385 to 371°C shown in figure 78 (c). There is sudden increase in yield strength from 1178 MPa to 1344 MPa as the temperature decreases from 371 to 343°C. This is due to the presence of tempered martensite phase along with the bainitic microstructure in 343°C austempered sample as shown in figure 42. In this sample same level of fraction of martensite or lower bainite phase is present-
Figure 78: Effect of width of (a) bainitic ferrite lath, (b) martensite or lower bainite lath, (c) islands of retained austenite, (d) tempered martensite lath on the yield strength of 0.3% C LCLA austempered samples.
- whereas bainitic ferrite fraction is lower compared to sample austempered at 371°C. Figure 78 (a) and (b) shows the slight but statistically significant increase in the lath size of bainitic ferrite and martensite or lower bainite phase in sample austempered at 343°C compared to 371°C. Normal trend is that as the lath size increases yield strength decreases. But it is hypothesized that due to the presence of tempered martensite phase, the effect of increase in lath sizes of these two phases did not show decrease in yield strength and the higher strength is due to the combined effect of phase fractions and lath sizes of all the phases present. Statistically similar volume fraction of bainitic ferrite is present in samples austempered at 343 and 316°C shown in figure 77. Whereas the tempered martensite volume fraction increases and martensite or lower bainite phase fraction decreases in sample austempered at 316°C compared to 343°C austempered sample. Lath sizes of bainitic ferrite and martensite or lower bainite were similar (figure 78 (a) and b)) but the lath size of tempered martensite increases in sample austempered at 316°C
compared to sample austempered at 343°C shown in figure 78 (d) and 70(d). The combined effect of phase fraction and the lath sizes had no effect on yield strength and similar level of yield strength (1344 and 1367 MPa) is found between these two samples. When the temperature decreases from 316 to 288°C, almost completely tempered martensitic microstructure is obtained along with films of retained austenite in 288°C compared to the mixed microstructure obtained in sample austempered at 316°C. The high volume fraction (≈ 95%) of tempered martensite resulted in the increase in strength shown in figure 77 but this difference in strength is not too high (1367 to 1411 MPa). Figure 78(d) and 70(d) also show the decrease in lath size of tempered martensite in sample austempered at 288°C compared to 316°C sample. Statistically similar yield strength observed between samples austempered at 288 and 260°C is due to the presence of similar volume fractions of tempered martensite and inter-lath retained austenite phases. The increase in lath size of tempered martensite in sample austempered 260°C compared to 288°C has no effect on yield strength shown in figure 78(d). Figure 78 (e) illustrates the effect of width of films of retained austenite on yield strength. Since inter-lath austenite widths in all the austempered samples were statistically similar, no conclusion could be drawn on the observed improved strength.

Similar effect of volume fractions and lath sizes of phases is observed on fracture toughness compared to the effect on yield strength for the samples austempered above 371°C. Fracture toughness increases from 80 to 105 MPa√m as the austempering temperature decreases from 399 to 371°C shown in figure 79. Volume fraction of islands of austenite decreases as the austempering temperature decreases from 399 to 371°C. Whereas variations of phase fractions of martensite or lower bainite and bainitic ferrite phases, as the temperature decreases from 399 to 371°C is illustrated in figure 79. As explained earlier, presence of islands of retained austenite is-
Figure 79: Effect of volume fraction of different phases on fracture toughness of 0.3% C LCLA steel. BF: Bainitic Ferrite, TM: Tempered Martensite, MA-LB: Martensite or lower bainite, IRA: Islands of Retained Austenite, RA: Films of Retained Austenite.

- also detrimental to the fracture toughness. Large stresses are present at the crack tip during the crack propagation in CT (compact tension) specimen. These unstable islands of retained austenite (compared to films of austenite) ahead of the crack tip transforms to martensite by stress induced transformation which result in poor fracture toughness. Figure 80 (a) and (b) shows the lath sizes of bainitic ferrite and martensite or lower bainite phases and they are statistically similar in the range of 371-399°C but the lath size of the islands of retained austenite decreases as shown in figure 80 (c). Combined effect of all these factors resulted in increase in fracture toughness.
Figure 80: Effect of width of a) bainitic ferrite lath, b) martensite or lower bainite lath, c) islands of retained austenite, d) tempered martensite lath on the fracture toughness of 0.3%C LCLA austempered samples.
The increase in fracture toughness of sample austempered at 343°C compared to 371°C austempered sample (105 to 139 MPa√m) is due to the presence of mixed microstructure (tempered martensite and bainitic ferrite microstructure). Samples austempered at 343 and 316°C consisted of mixed microstructures but the tempered martensite volume fraction was higher in the sample austempered at 316 compared to the 343°C sample. Whereas martensite or lower bainite phase fraction decreases as the austempering temperature decreases from 343 to 316°C. Both of these samples have statistically similar level of fracture toughness shown in figure 79.

From the figure 80 (d) and 70 (d) it is evident that the lath size of tempered martensite increases as the temperature decreases from 343 to 316°C. The increase in lath size of tempered martensite phase did not result in change in fracture toughness, as the tempered martensite volume fractions were significantly different in these samples. Figure 80 a) and b) shows statistically similar lath sizes of bainitic ferrite and martensite or lower bainite in samples austempered at 316 and 343°C. Sample austempered at 288°C has almost completely tempered martensitic microstructure and it
showed statistically similar fracture toughness as that of samples austempered at 343 and 316°C (figure 79). As pointed out earlier these three austempering temperature (343, 316 and 288°C) resulted in optimum combination of mechanical properties in 0.3%C LCLA steel. As the austempering temperature decreases from 288 to 260°C, fracture toughness decreases from 133 to 107 MPa√m. These two samples have similar level of volume fractions of tempered martensite and films of retained austenite shown in figure 79. From figure 77 and 79, it is evident that the similar fractions present in these two samples (288 and 260°C) have resulted in no change in yield strength but the fracture toughness has decreased drastically. This can be attributed to the statistically significant increase in lath size of the tempered martensite phase as the temperature decreases from 288 to 260°C (Figure 80 (d) and 70 (d)). Moreover statistically similar volume fractions and width of films of retained austenite are present in these two samples (figure 80 (e)). Clearly, when the phase fractions are similar, the decrease in lath size has a major effect on fracture toughness compared to the yield strength and the finer lath microstructure has a greater degree of resistance for crack propagation.

Figure 81 a)-g) shows the fractographs of austempered samples. The fractographs of sample austempered at 316 and 343°C shows only dimpled fracture and all the other samples show varying degree of both quasi-cleavage and dimpled ductile fracture. The sample austempered at 260 and 288°C shows the higher degree of dimpled fracture and less quasi-cleave type of fracture. Above austempering temperature of 371°C all the samples showed higher degree of quasi-cleavage fracture and increased amount of quasi-cleavage fracture was observed in sample austempered at 399°C. Fractographs indications are in good agreement with the observed fracture toughness values. This steel resulted in tensile strength in the range of 1302-1658MPa and fracture toughness in the range of 80-139MPa√m, which makes it third generation
Figure 81: Fractographs obtained from the fractured surface of Compact Tension (CT) specimen 0.3\%C LCLA samples austempered at a) 260\(^\circ\)C, b) 288\(^\circ\)C, c) 316\(^\circ\)C, d) 343\(^\circ\)C respectively. QF - quasi cleavage fracture, DF- Dimpled ductile fracture.
Figure 81 Fractographs obtained from the fractured surface of Compact Tension (CT) specimen 0.3\%C LCLA samples austempered at e) 371°C, f) 385°C, g) 399°C respectively. QF - quasi cleavage fracture, DF - Dimpled ductile fracture
- generation advanced high strength steel. Figure 8.2 shows the comparison of yield strength of 0.2C and 0.3%C LCLA austempered samples. From the graph it is evident that, the single step and two step austempering resulted in similar levels of yield strength in 0.2%C LCLA steel samples and as the austempering temperature decreases yield strength increases. Significant increase in the yield strength of 0.3%C LCLA austempered samples is observed when compared to 0.2%C LCLA austempered samples. In general, in plain carbon steel, as the carbon content increases, the strength of the alloy increases by solid solution strengthening. This effect along with finer microstructure of bainitic ferrite and tempered martensite (above and below $M_s$ temperature) in 0.3%C LCLA steel resulted in higher yield strength for these samples compared to 0.2%C LCLA steel.

![Graph showing comparison of yield strength](image)

Figure 8.2: Comparison of yield strength of 0.2C and 0.3%C LCLA austempered samples.
Figure 83: Comparison of tensile strength of 0.2C and 0.3%C LCLA austempered samples.

Figure 84: Comparison of fracture toughness of 0.2C and 0.3%C LCLA austempered samples.
Figure 83 shows the tensile strength of 0.2 and 0.3%C LCLA steel austempered samples and low degree of difference in ultimate tensile strengths (in the range of 1293 to 1358MPa) is observed in samples austempered above 371°C in both 0.2 and 0.3%C LCLA steels. But as the austempering decreases there is significant difference in ultimate tensile strengths. Figure 84 shows the comparison of fracture toughness values of 0.2C and 0.3%C LCLA austempered samples. 0.2%C LCLA two step austempered samples show statistical significant increase in fracture toughness compared to single step austempered samples. As the austempering temperature decreases fracture toughness increases and reaches maximum at the lowest austempering temperature for both single and two step heat treatment. Whereas for 0.3%C LCLA steel there is a maximum point in the fracture toughness curve with respect to austempering temperature between 316 and 343°C. These samples consisted of mixture of tempered martensite, bainitic ferrite, martensite or lower bainite and retained austenite.

In summary, austempering process and the designed composition resulted in desired bainitic ferrite and austenite (above Mₘᵢₙ) and tempered martensite and austenite (below Mₘᵢₙ) microstructures in 0.2C and 0.3%C LCLA steels. Mixed microstructure was observed in 0.3%C LCLA samples austempered between 316 and 343°C which imparted exceptional combination of high strength and toughness to the steel. Mixed microstructure and the tempered martensite microstructure yielded high strength and toughness to the steel compared to the bainitic microstructure. But the yield strength and fracture toughness obtained in all the austempered samples (both 0.2C and 0.3%C LCLA) were higher than the first generation advanced high strength steels. Variations in mechanical properties with respect to austempering temperature are explained with the help of measured volume fractions of different phases and their lath sizes.
CHAPTER 7. CONCLUSIONS

- Two new third generation advanced high strength steels (0.2%C LCLA and 0.3%C LCLA) with exceptional combination of high strength and high toughness has been developed.

- Low amounts of elements Ni, Cr, Mn, Mo in these two steels imparted sufficient hardenability to produce bainitic ferrite and tempered martensite microstructure without any formation of proeutectoid ferrite and pearlite.

- Bainitic ferrite and high carbon austenite microstructure along with martensite or lower bainite phase was obtained in samples of 0.2%C LCLA steel austempered above $M_s$ temperature. Below $M_s$ temperature samples showed tempered martensite and austenite microstructure.

- In 0.3%C LCLA, the austempered samples consisted of tempered martensite and austenite microstructure below $M_s$ temperature, and bainitic ferrite, austenite along with martensite or lower bainite microstructure above $M_s$ temperature. The samples austempered at 316 and 343°C showed the presence of all the four phases bainitic ferrite, tempered martensite, high carbon austenite and martensite or lower bainite.

- TEM analysis confirmed the presence of films of retained austenite in between the bainitic ferrite laths and tempered martensite laths. Bainitic ferrite showed sheaf morphology and the tempered martensite laths showed the presence of carbide precipitates.

- Retained austenite in all the austempered samples was sufficiently enriched with carbon content (>1wt %)
Yield strength, tensile strength and fracture toughness increases as the austempering temperature decreases in 0.2\%C LCLA. But the ductility increases with increase in austempering temperature.

Single step austempering yielded tensile strength in the range of 1293-1392MPa and fracture toughness in the range of 54-114MPa√m. The lower range of mechanical properties was obtained due to bainitic ferrite and austenite microstructure, whereas the higher range mechanical properties was due to tempered martensite and austenite microstructure. Nonetheless both these microstructures imparted properties which are higher than first generation advanced high strength steels.

The presence of martensite or lower bainite phase along with bainitic ferrite and austenite resulted in improved mechanical properties.

Two step austempering resulted in tensile strength in the range of 1276-1402MPa and fracture toughness in the range of 97-141MPa√m. Two step austempering did not have any significant improvement on yield strength compared to single step austempering. But the two step heat treatment imparted higher fracture toughness to 0.2\%C LCLA steel compared to single step heat treatment.

0.3\%C LCLA steel had higher mechanical properties when compared to 0.2\%C LCLA single and two step austempered samples.

In 0.3\%C LCLA Yield strength, tensile strength increases as the austempering temperature decreases. Fracture toughness increases as the austempering temperature decreases and reaches a maximum value between 316 and 343\°C and decreases below 316\°C austempering temperature.
• Single step austempering of 0.3%C LCLA resulted in tensile strength in the range of 1302 -1658MPa and fracture toughness in the range of 80-139MPa√m.

• The Highest combination of strength and toughness were obtained in samples over the temperature range of 260-343°C in 0.3%C LCLA steel. These property combinations were similar in this temperature range which shows that 0.3%C LCLA steel has a robust envelope to obtain the optimal properties.

• As the bainitic ferrite fraction decreases and the martensite or lower bainite fraction increases the mechanical properties of both 0.2 and 0.3%C LCLA steels increases.

• Presence of higher amount of islands of retained austenite in sample austempered above 371°C resulted in lower mechanical properties and as the volume fraction decreases the mechanical properties increases in 0.3%C LCLA steel.

• As the lath sizes of bainitic ferrite, martensite or lower bainite and islands of retained austenite decreases, yield strength, fracture toughness increases in samples austempered above 371°C in both 0.2 and 0.3%C LCLA steels.

• Mixed microstructure present in samples austempered at 316 and 343°C in 0.3%C LCLA resulted in the highest mechanical properties and this was due to the combined effect of volume fraction and lath size variation in these two samples.

• Changes in lath sizes of different phases have higher effect on fracture toughness compared to yield strength in both 0.2 and 0.3%C LCLA steels.
CHAPTER 8. FUTURE WORK

Further research can be carried out on these two steels to enhance the mechanical properties. Even though the strength and fracture toughness levels are high in these alloys, their %elongation values are below 10%. Ductility can be further enhanced by using different heat treatment method such as continuous cooling in the bainitic region, which may result in finer bainitic ferrite microstructure. Due to the faster cooling rate, large undercooling is available which may increase the fraction of bainitic ferrite and the islands of retained austenite fraction can be reduced. The 0.2%C LCLA steel has a higher hardenability (figure 16) hence different cooling rates can be used to obtain bainite by avoiding the ferrite pearlite transformation. In this investigation the average bainitic ferrite lath size of 0.3µm was obtained by austempering for two hours. It is possible to reduce the lath size by decreasing the prior austenite grain size. By reducing the grain size more nucleation sites and nucleation rates can be obtained for bainitic ferrite formation which will result in finer microstructure. The austenite grain size can be reduced by applying thermomechanical treatment during austenitization. 0.2%C LCLA has grain refining elements Nb and V and presence of these elements along with thermomechanical treatment can further help in reduction of austenite grain size. Austempering time of 2 hours is used for all the samples, which may not be a attractive feature when it comes for industrial applications. Hence research can also be carried out by heat treating for lesser austempering time and study the effects on properties. Other attractive material properties such as weldability, formability, bendability and stretch flangeability which are of utmost important for automotive industries can be explored further in these two steels.
APPENDIX A

Ballistic resistance of 0.3%C LCLA Steel

Ballistic testing

One of the potential applications of the currently designed steel is for the armor plate for military vehicle. Highest combination of strength and toughness were obtained for the 0.3%C LCLA steel austempered between 260-343°C. Among these heat treated conditions, the sample austempered at 316°C had the best property combinations and hence it was chosen for the preliminary qualitative ballistic test. Two target plates of dimensions of 203 x 178 x 25 mm (8” x 7” x 1”) were obtained from 0.3%C LCLA steel in the forged and rolled condition (as explained in section 5.1) and austempered at 316°C for two hours. A third target plate of mild steel alloy (44W compliant to CSA-G40.21) of same dimension was used for comparison purposes. High speed projectiles were made to hit these 3 plates and the results are compared. The ballistic tests were performed at the High-Speed Impact Research and Technology Facility of the Planetary and Space Science Centre, University of New Brunswick, Canada, using a Two-Stage Light Gas Gun (Figure A1).

Figure A.1: UNB's Two-Stage Light Gas Gun Facility.
Mild steel Fragment Simulating Projectiles (FSP) were used to conduct the ballistic tests and are shown in Figure A.2 (a) and described fully in [113]. Figure A.2 (b) shows the target plates mounted in the blast chamber using a clamp plate setup.

![Figure A.2: a) Mild steel Fragment Simulating Projectile (FSP) with launch sabot. b) Sample test plate target clamp arrangement.](image)

Using Laser-Trap (LT), High-Speed Video (HSV) and Framing Camera data, Projectile integrity, velocity and alignment measurements were obtained. Ballistic test was conducted at room temperature and ambient atmosphere. First shot was fired at the mild steel target and the mass, dimension and speed of the projectile are reported in table A.1. Second shot was fired at the first 316°C AHSS plate at almost same speed of 687m/s and the third shot was fired at the second plate with a higher speed of 925m/s (table A.1). Figure A.3 shows the high speed camera images to see the misalignments of the shot projectiles for mild steel and AHSS target plates. Figure A.3 a) shows that the FSP hit the target with very minimal misalignment. Figure A.3 b) shows the projectile just before it hit the target; and the FSP was intact and impacted the target plate with
Figure A.3 a) FSP Shot 1 into mild steel target plate. b) FSP Shot 2 into treated steel (316°C) target plate. c) FSP Shot 3 into treated steel (316°C) target plate.

~7° pitch and no yaw Figure A.3c) shows that the projectile was intact and impacted the target plate with an angular misalignment of -4° pitch and no yaw. After the tests the target plates were visually examined and compared with mild steel plates for damage.
Table A.1: Ballistic test parameters.

<table>
<thead>
<tr>
<th>Shot</th>
<th>Projectile diameter and material</th>
<th>Projectile mass (g)</th>
<th>Impact velocity (m/s)</th>
<th>Target (see text for details)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shot 1</td>
<td>20 mm, mild steel</td>
<td>53.0</td>
<td>693</td>
<td>Mild steel</td>
</tr>
<tr>
<td>Shot 2</td>
<td>20 mm (0.78 caliber), mild steel</td>
<td>52.7</td>
<td>687</td>
<td>3rd generation AHSS (316°C)</td>
</tr>
<tr>
<td>Shot 3</td>
<td>20 mm, mild steel</td>
<td>52.9</td>
<td>925</td>
<td>3rd generation AHSS (316°C)</td>
</tr>
</tbody>
</table>

**Post-Ballistic mechanical properties**

To study the effect of impact of FSP on mechanical properties, from the impact areas of the AHSS plates, four compact tension and four cylindrical tensile samples were prepared and tested in accordance with the ASTM standards (Sections 5.5 and 5.6).

**Ballistic resistance**

Figure A.4 shows the damaged mild steel plate and the projectile (FSP) was completely embedded in the plate. Figure A.4 a) also shows the target material displacement along with a discolored ring indicating that the impact created high amount of energy which is converted into heat. Whereas the 316°C AHSS shows very little damage and a small dent is formed in the test plate shown in figure A.5 b). The projectile was completely shattered and there is absence of discolored ring in the AHSS plate. The third shot with higher speed 925m/s showed similar results but analysis of compression deformation due to the impact was not carried out for these two AHSS plates. From this limited qualitative study it can be concluded that the 0.3%C LCLA -
Figure A.4: Post-Ballistic condition of projectile and mild steel target plate (shot 1).

(a)  (b)

Figure A.5: Post-Ballistic condition of projectile and heat treated steel (316°C) target plate (shot 2). The at-target velocities (693 m/s and 925 m/s, respectively).

(a)  (b)

- AHSS absorb impact energy compared to mild steel. Additional tests need to be carried out (following the protocols in STANAG 4162 or MIL-DTL-12560J) to determine if the LCLA steel is suitable for armored vehicle applications.
Post-Ballistic Properties

Table A.2 reports the mechanical properties of 0.3% C LCLA steel before and after the ballistic test. Statistically significant difference is observed between the pre and post ballistic test samples. Yield strength, tensile strength and fracture toughness and hardness values are reduced in the post ballistic samples. Moreover, there is a slight increase in the ductility in the post ballistic sample. Even though the strength is reduced, the steel is still desirable due to these high properties (YS-1133MPa, UTS-1311 and Fracture toughness– 109MPa√m).

Table A.2: Comparison of the mechanical properties of the 0.3%C LCLA samples austempered at 316°C before and after ballistic testing.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value Before Ballistic Test</th>
<th>Value After Ballistic Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness (HRC)</td>
<td>44.6 ± 0.4</td>
<td>41.3 ± 0.9</td>
</tr>
<tr>
<td>Yield Strength (MPa)</td>
<td>1367 ± 6</td>
<td>1133 ± 32</td>
</tr>
<tr>
<td>Ultimate Strength (MPa)</td>
<td>1548 ± 7</td>
<td>1311 ± 27</td>
</tr>
<tr>
<td>Fracture Toughness (MPa√m)</td>
<td>137 ± 3</td>
<td>109 ± 5</td>
</tr>
<tr>
<td>Strain hardening exponent (n)</td>
<td>0.12 ± 0.01</td>
<td>0.09 ± 0.01</td>
</tr>
<tr>
<td>% Elongation</td>
<td>5.9 ± 0.1</td>
<td>8.3 ± 1.8</td>
</tr>
</tbody>
</table>

The heat generated during the impact is retained in the sample and the sample undergoes severe deformation, this results in the formation of adiabatic shear bands (ASB) [114]. The formation of ASBs decreases the strength and toughness of the alloy, resulting in a softened material, which explains the reduction in strength, toughness and increment in the ductility of samples taken from the impact area. Figure A.6 a) and b) shows the microstructure of the 316°C austempered sample and the microstructure of the sample prepared from the impact area for
comparison. Both the figures show the presence of tempered martensite and retained austenite and there is not much difference between these two microstructures.

Figure A.6: Microstructure of sample austempered at 316°C a) before ballistic test b) after ballistic test.
APPENDIX B

Diffraction pattern indexing details

Table B.1: Diffraction pattern indexing details of 0.2%C LCLA sample austempered at 371°C (Figure. 48)

<table>
<thead>
<tr>
<th>Spot</th>
<th>Measured d spacing (Å)</th>
<th>(hkl)</th>
<th>Calculated d spacing (Å)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.114</td>
<td>α_b(110)</td>
<td>2.029</td>
<td>4.19</td>
</tr>
<tr>
<td>2</td>
<td>1.481</td>
<td>α_b(200)</td>
<td>1.435</td>
<td>3.21</td>
</tr>
<tr>
<td>3</td>
<td>2.096</td>
<td>α_b(110)</td>
<td>2.029</td>
<td>3.30</td>
</tr>
<tr>
<td>4</td>
<td>1.474</td>
<td>α_b(0120)</td>
<td>1.435</td>
<td>2.72</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Spot</th>
<th>Measured d spacing (Å)</th>
<th>(hkl)</th>
<th>Calculated d spacing (Å)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.126</td>
<td>γ(111)</td>
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<tr>
<td>2</td>
<td>1.859</td>
<td>γ(200)</td>
<td>1.799</td>
<td>3.34</td>
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</table>

<table>
<thead>
<tr>
<th>Angles</th>
<th>Measured angle (°)</th>
<th>hkl</th>
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<th>% difference</th>
</tr>
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<tbody>
<tr>
<td>1∠2</td>
<td>44.43</td>
<td>α_b(110)</td>
<td>α_b(200)</td>
<td>45</td>
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<tr>
<td>2∠3</td>
<td>46.06</td>
<td>α_b(200)</td>
<td>α_b(1110)</td>
<td>45</td>
</tr>
<tr>
<td>3∠4</td>
<td>44.94</td>
<td>α_b(110)</td>
<td>α_b(0120)</td>
<td>45</td>
</tr>
<tr>
<td>4∠1</td>
<td>44.57</td>
<td>α_b(0120)</td>
<td>α_b(1110)</td>
<td>45</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Angles</th>
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<th>hkl</th>
<th>Calculated angle (°)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1∠2</td>
<td>51.97</td>
<td>γ(111)</td>
<td>γ(200)</td>
<td>54.73</td>
</tr>
</tbody>
</table>
Table B.2: Diffraction pattern indexing details of 0.3% C LCLA sample austempered at 260°C (Figure.49)

<table>
<thead>
<tr>
<th>Spot</th>
<th>Measured d spacing (Å)</th>
<th>(hkl)</th>
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<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.212</td>
<td>α'(211)</td>
<td>1.1717</td>
<td>3.44</td>
</tr>
<tr>
<td>2</td>
<td>0.802</td>
<td>α'(123)</td>
<td>0.767</td>
<td>4.56</td>
</tr>
<tr>
<td>3</td>
<td>1.219</td>
<td>α'(112)</td>
<td>1.1717</td>
<td>4.04</td>
</tr>
<tr>
<td>4</td>
<td>0.947</td>
<td>α'(301)</td>
<td>0.9076</td>
<td>4.34</td>
</tr>
<tr>
<td>5</td>
<td>0.938</td>
<td>α'(310)\text{II}</td>
<td>0.9076</td>
<td>3.35</td>
</tr>
<tr>
<td>6</td>
<td>0.871</td>
<td>α'(222)\text{II}</td>
<td>0.828</td>
<td>5.19</td>
</tr>
<tr>
<td>7</td>
<td>1.228</td>
<td>α'(112)\text{II}</td>
<td>1.1717</td>
<td>4.80</td>
</tr>
<tr>
<td>8</td>
<td>0.670</td>
<td>α'(402)\text{II}</td>
<td>0.642</td>
<td>4.36</td>
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Diffraction pattern indexing details of 0.3% C LCLA sample austempered at 260°C (Figure.49)

<table>
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<th>% difference</th>
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<td>Fe₃C(020)</td>
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</table>
Diffraction pattern indexing details of 0.3\%C LCLA sample austempered at 260°C (Figure.49)

<table>
<thead>
<tr>
<th>Angles</th>
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<th>hkl</th>
<th>Calculated angle (°)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1∠2</td>
<td>39.60</td>
<td>α'(211) ∠ α'(123)</td>
<td>40.20</td>
<td>1.49</td>
</tr>
<tr>
<td>2∠3</td>
<td>39.59</td>
<td>α'(123) ∠ α'(112)</td>
<td>40.20</td>
<td>1.52</td>
</tr>
<tr>
<td>3∠4</td>
<td>50.97</td>
<td>α'(112) ∠ α'(301)</td>
<td>49.79</td>
<td>2.37</td>
</tr>
<tr>
<td>4∠1</td>
<td>49.84</td>
<td>α'(301) ∠ α' (2 1 1)</td>
<td>49.79</td>
<td>0.10</td>
</tr>
<tr>
<td>5∠6</td>
<td>42.75</td>
<td>α'(310) ∥ ∠ α'(222) ∥</td>
<td>43.09</td>
<td>0.79</td>
</tr>
<tr>
<td>6∠7</td>
<td>62.65</td>
<td>α'(222) ∥ ∠ α'(112) ∥</td>
<td>61.87</td>
<td>1.26</td>
</tr>
<tr>
<td>7∠8</td>
<td>42.92</td>
<td>α'(112) ∥ ∠ α'(402) ∥</td>
<td>43.08</td>
<td>0.37</td>
</tr>
<tr>
<td>8∠5</td>
<td>31.68</td>
<td>α'(402) ∥ ∠ α'(310)</td>
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</table>

Table.B.3: Diffraction pattern indexing details of 0.3\%C LCLA sample austempered at 260°C (Figure.50)

<table>
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<tr>
<th>Spot</th>
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<th>(hkl)</th>
<th>Calculated d spacing (Å)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.926</td>
<td>α'(310)</td>
<td>0.9076</td>
<td>2.03</td>
</tr>
<tr>
<td>2</td>
<td>1.192</td>
<td>α'(211)</td>
<td>1.1717</td>
<td>1.73</td>
</tr>
<tr>
<td>3</td>
<td>1.214</td>
<td>α'(121)</td>
<td>1.1717</td>
<td>3.87</td>
</tr>
<tr>
<td>4</td>
<td>0.578</td>
<td>α'(431)</td>
<td>0.563</td>
<td>2.66</td>
</tr>
<tr>
<td>5</td>
<td>1.195</td>
<td>α'(211) ∥</td>
<td>1.1717</td>
<td>1.99</td>
</tr>
<tr>
<td>6</td>
<td>0.788</td>
<td>α'(132) ∥</td>
<td>0.767</td>
<td>2.74</td>
</tr>
<tr>
<td>7</td>
<td>1.212</td>
<td>α'(121) ∥</td>
<td>1.1717</td>
<td>3.44</td>
</tr>
<tr>
<td>8</td>
<td>0.938</td>
<td>α'(310) ∥</td>
<td>0.9076</td>
<td>3.35</td>
</tr>
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</table>
Diffraction pattern indexing details of 0.3%C LCLA sample austempered at 260°C (Figure.50)

<table>
<thead>
<tr>
<th>Spot</th>
<th>Measured d spacing (Å)</th>
<th>(hkl)</th>
<th>Calculated d spacing (Å)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.303</td>
<td>γ(220)</td>
<td>1.272</td>
<td>2.44</td>
</tr>
<tr>
<td>2</td>
<td>1.319</td>
<td>γ(202)</td>
<td>1.272</td>
<td>3.69</td>
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Diffraction pattern indexing details of 0.3%C LCLA sample austempered at 260°C (Figure.50)

<table>
<thead>
<tr>
<th>Angles</th>
<th>Measured angle (°)</th>
<th>hkl</th>
<th>Calculated angle (°)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1∠2</td>
<td>48.78</td>
<td>α'(310) ∠ α'(211)</td>
<td>49.79</td>
<td>2.03</td>
</tr>
<tr>
<td>2∠3</td>
<td>81.77</td>
<td>α'(211) ∠ α'(121)</td>
<td>80.40</td>
<td>1.70</td>
</tr>
<tr>
<td>3∠4</td>
<td>28.16</td>
<td>α'(121) ∠ α'(431)</td>
<td>28.27</td>
<td>0.39</td>
</tr>
<tr>
<td>4∠1</td>
<td>21.29</td>
<td>α'(431) ∠ α'(310)</td>
<td>21.52</td>
<td>1.07</td>
</tr>
<tr>
<td>5∠6</td>
<td>39</td>
<td>α'(211)∥ ∠ α'(132)∥</td>
<td>40.20</td>
<td>2.99</td>
</tr>
<tr>
<td>6∠7</td>
<td>39.91</td>
<td>α'(132)∥ ∠ α'(121)∥</td>
<td>40.20</td>
<td>0.72</td>
</tr>
<tr>
<td>7∠8</td>
<td>51.83</td>
<td>α'(121)∥ ∠ α'(310)∥</td>
<td>49.79</td>
<td>4.10</td>
</tr>
<tr>
<td>8∠5</td>
<td>49.26</td>
<td>α'(310)∥ ∠ α'(2 1 1)</td>
<td>49.79</td>
<td>1.06</td>
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</table>

<table>
<thead>
<tr>
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<th>Measured angle (°)</th>
<th>hkl</th>
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<th>% difference</th>
</tr>
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<tbody>
<tr>
<td>1∠2</td>
<td>57.89</td>
<td>γ(220) ∠ γ(202)</td>
<td>60</td>
<td>3.52</td>
</tr>
</tbody>
</table>
Table B.4: Diffraction pattern indexing details of 0.3\%C LCLA sample austempered at 343°C (Figure.51)

<table>
<thead>
<tr>
<th>Spot</th>
<th>Measured d spacing (Å)</th>
<th>(hkl)</th>
<th>Calculated d spacing (Å)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.203</td>
<td>α_b(112)</td>
<td>1.1717</td>
<td>2.67</td>
</tr>
<tr>
<td>2</td>
<td>0.782</td>
<td>α_b(132)</td>
<td>0.767</td>
<td>1.95</td>
</tr>
<tr>
<td>3</td>
<td>1.474</td>
<td>α_b(020)</td>
<td>1.435</td>
<td>2.72</td>
</tr>
<tr>
<td>4</td>
<td>1.228</td>
<td>α_b(1 1 2 )</td>
<td>1.1717</td>
<td>4.80</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Spot</th>
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<th>(hkl)</th>
<th>Calculated d spacing (Å)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.086</td>
<td>γ(111)</td>
<td>2.078</td>
<td>0.38</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Angles</th>
<th>Measured angle (°)</th>
<th>hkl</th>
<th>Calculated angle (°)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1∠2</td>
<td>28.78</td>
<td>α_b(112) ≤ α_b(132)</td>
<td>29.21</td>
<td>1.47</td>
</tr>
<tr>
<td>2∠3</td>
<td>35.79</td>
<td>α_b(132) ≤ α_b(020)</td>
<td>36.70</td>
<td>2.48</td>
</tr>
<tr>
<td>3∠4</td>
<td>66.82</td>
<td>α_b(020) ≤ α_b(1 1 2 )</td>
<td>65.91</td>
<td>1.38</td>
</tr>
<tr>
<td>4∠1</td>
<td>49.05</td>
<td>α_b(1 1 2 ) ≤ α_b(1 1 2 )</td>
<td>48.19</td>
<td>1.78</td>
</tr>
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</table>
Table B.5: Diffraction pattern indexing details of 0.3%C LCLA sample austempered at 371°C (Figure 52).

<table>
<thead>
<tr>
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<th>Measured d spacing (Å)</th>
<th>(hkl)</th>
<th>Calculated d spacing (Å)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.089</td>
<td>α_b(110)</td>
<td>2.029</td>
<td>2.96</td>
</tr>
<tr>
<td>2</td>
<td>1.212</td>
<td>α_b(112)</td>
<td>1.1717</td>
<td>3.44</td>
</tr>
<tr>
<td>3</td>
<td>1.485</td>
<td>α_b(002)</td>
<td>1.435</td>
<td>3.48</td>
</tr>
<tr>
<td>4</td>
<td>1.199</td>
<td>α_b(112)</td>
<td>1.1717</td>
<td>2.33</td>
</tr>
<tr>
<td>5</td>
<td>1.215</td>
<td>α_{bII}(112)</td>
<td>1.1717</td>
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</tr>
<tr>
<td>6</td>
<td>1.227</td>
<td>α_{bII}(211)</td>
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</table>

<table>
<thead>
<tr>
<th>Angles</th>
<th>Measured angle (°)</th>
<th>hkl</th>
<th>Calculated angle (°)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1∠2</td>
<td>54.24</td>
<td>α_b(110) ⋯ α_b(112)</td>
<td>54.73</td>
<td>0.90</td>
</tr>
<tr>
<td>2∠3</td>
<td>36.05</td>
<td>α_b(112) ⋯ α_b(002)</td>
<td>35.26</td>
<td>2.24</td>
</tr>
<tr>
<td>3∠4</td>
<td>35.49</td>
<td>α_b(002) ⋯ α_b(112)</td>
<td>35.26</td>
<td>2.24</td>
</tr>
<tr>
<td>4∠1</td>
<td>54.22</td>
<td>α_b(112) ⋯ α_b(211)</td>
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<td>33.86</td>
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<td>33.55</td>
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</table>
Table B.6: Diffraction pattern indexing details of 0.3%C LCLA sample austempered at 399°C (Figure 53).

<table>
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</thead>
<tbody>
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<td>0.9076</td>
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</tr>
<tr>
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<td>1.195</td>
<td>α₆(112)</td>
<td>1.1717</td>
<td>1.98</td>
</tr>
<tr>
<td>3</td>
<td>0.804</td>
<td>α₆(123)</td>
<td>0.767</td>
<td>4.82</td>
</tr>
<tr>
<td>4</td>
<td>1.242</td>
<td>α₆(211)</td>
<td>1.1717</td>
<td>5.99</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Spot</th>
<th>Measured d spacing (Å)</th>
<th>(hkl)</th>
<th>Calculated d spacing (Å)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>1.2724</td>
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<table>
<thead>
<tr>
<th>Angles</th>
<th>Measured angle (°)</th>
<th>hkl</th>
<th>Calculated angle (°)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1∠2</td>
<td>49.16</td>
<td>α₆(301) ∠ α₆(112)</td>
<td>49.79</td>
<td>1.26</td>
</tr>
<tr>
<td>2∠3</td>
<td>39.05</td>
<td>α₆(112) ∠ α₆(123)</td>
<td>40.20</td>
<td>2.86</td>
</tr>
<tr>
<td>3∠4</td>
<td>42.05</td>
<td>α₆(123) ∠ α₆(211)</td>
<td>40.20</td>
<td>4.60</td>
</tr>
<tr>
<td>4∠1</td>
<td>49.74</td>
<td>α₆(211) ∠ α₆(301)</td>
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<td>0.1</td>
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</table>
Table B.7: Diffraction pattern indexing details of 0.3% C LCLA sample austempered at 399°C (Figure 54).

<table>
<thead>
<tr>
<th>Spot</th>
<th>Measured d spacing (Å)</th>
<th>(hkl)</th>
<th>Calculated d spacing (Å)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.199</td>
<td>α_b(112)</td>
<td>1.1717</td>
<td>2.32</td>
</tr>
<tr>
<td>2</td>
<td>0.850</td>
<td>α_b(222)</td>
<td>0.8285</td>
<td>2.59</td>
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<tr>
<td>3</td>
<td>0.944</td>
<td>α_b(310)</td>
<td>0.9076</td>
<td>4.01</td>
</tr>
<tr>
<td>4</td>
<td>0.675</td>
<td>α_b(402)</td>
<td>0.6418</td>
<td>5.17</td>
</tr>
<tr>
<td>5</td>
<td>1.219</td>
<td>α_bII(112)</td>
<td>1.1717</td>
<td>4.04</td>
</tr>
<tr>
<td>6</td>
<td>1.185</td>
<td>α_bII(121)</td>
<td>1.1717</td>
<td>1.14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Spot</th>
<th>Measured d spacing (Å)</th>
<th>(hkl)</th>
<th>Calculated d spacing (Å)</th>
<th>% difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.134</td>
<td>γ(111)</td>
<td>2.078</td>
<td>2.69</td>
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</table>

<table>
<thead>
<tr>
<th>Angles</th>
<th>Measured angle (°)</th>
<th>hkl</th>
<th>Calculated angle (°)</th>
<th>% difference</th>
</tr>
</thead>
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<tr>
<td>1∠2</td>
<td>60.61</td>
<td>α_b(112) (\neq) α_b(222)</td>
<td>61.87</td>
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<tr>
<td>2∠3</td>
<td>43.6</td>
<td>α_b(222) (\neq) α_b(310)</td>
<td>43.09</td>
<td>1.18</td>
</tr>
<tr>
<td>3∠4</td>
<td>32.19</td>
<td>α_b(310) (\neq) α_b(402)</td>
<td>31.94</td>
<td>0.78</td>
</tr>
<tr>
<td>4∠1</td>
<td>43.6</td>
<td>α_b(402) (\neq) α_b(112)</td>
<td>43.09</td>
<td>1.18</td>
</tr>
<tr>
<td>5∠6</td>
<td>81.42</td>
<td>α_bII(112) (\neq) α_bII(121)</td>
<td>80.41</td>
<td>1.26</td>
</tr>
</tbody>
</table>
REFERENCES


43. E.C. Bain, Alloying elements in steel. ASM, Ohio, USA, 1939.


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ABSTRACT

DEVELOPMENT OF HIGH STRENGTH HIGH TOUGHNESS THIRD GENERATION ADVANCED HIGH STRENGTH STEELS

by

CODRICK JOHN MARTIS

August 2015

Advisor: Prof. Susil K. Putatunda

Major: Materials Science and Engineering

Degree: Doctor of Philosophy

Third generation advanced high strength steels (AHSS’s) are emerging as very important engineering materials for structural applications. These steels have high specific strength and thus will contribute significantly to weight reduction in automotive and other structural component. In this investigation two such low carbon low alloy steels (LCLA) with high silicon content (1.6-2wt %) has been developed. These two steel alloys were subjected to single step and two step austempering in the temperature range of 260-399°C to obtain desired microstructures and mechanical properties. Austempering heat treatment was carried out for 2 hours in a molten salt bath. The microstructures were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and optical metallography. Quantitative analysis was carried out by image analysis technique. The effect of austempering temperature on the mechanical properties of these two alloys was examined. The influence of microstructures on the mechanical properties of alloys was also studied.

Austempering heat treatment resulted in fine carbide free bainitic ferrite and high carbon austenite microstructure in the samples austempered above $M_s$ temperature, whereas tempered martensite and austenite microstructure was obtained in samples austempered below $M_s$. 
temperature. Yield strength, tensile strength and fracture toughness were found to increase as the austempering temperature decreases, whereas ductility increases as the austempering temperature increases. Tensile strength in the range of 1276MPa -1658 MPa and the fracture toughness in the range of 80-141MPa√m were obtained in these two steels. Volume fractions of different phases present and their lath sizes are related to the mechanical properties. Austempered samples consisting of mixed microstructure of bainitic ferrite and tempered martensite phases resulted in the exceptional combination of strength and toughness.
AUTOBIOGRAPHICAL STATEMENT

I’m a final year graduate student completing my Ph.D. in Materials Science and Engineering from Wayne State University, Detroit, Michigan. I received my M.Tech. in Materials Engineering from National Institute of Technology, Surathkal, Karnataka, India, in July 2009 and B.E in Mechanical Engineering from Sri Jayachamarajendra College of Engineering, Mysore, Karnataka, India, in July 2006. I came to U.S.A. in 2009 to pursue my Ph.D. and my research has been focused on developing third generation advanced high strength steels.

I have a passion for playing piano and guitar and I’m a huge fan of classic rock and classical music. I have the hobby of making piano and guitar cover versions of famous songs composed by famous artists. I have a YouTube Channel where I upload my cover versions of songs (https://www.youtube.com/user/codrick24).