Manufacture and Properties of TWIP Steels with a Carbon Gradient

by

Mohamad Irwan Yahaya

Submitted in fulfilment of the requirement for the degree of
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Deakin University
June 2014
I am the author of the thesis entitled

Manuacture and Properties of TWIP Steels with a Carbon Gradient

submitted for the degree of Doctor of Philosophy (Engineering)

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Irwan Yahaya

June 2014
Abstract

Recent developments of high manganese Fe-Mn based Twinning Induced Plasticity (TWIP) steels for the automotive industry have been driven by the demand to increase ductility without compromising strength. TWIP steels show a unique combination of mechanical properties with moderate yield strengths (350 to 450 MPa), ultimate tensile strengths greater than 1000 MPa and uniform elongations of 50 to 60%.

The present research aims to ease the manufacture of this type of steel without diminishing its mechanical properties. The work uses carburizing, which introduces carbon into the steel surface after it has been processed into sheet. Carburizing was carried out by exposing steel to a carbon rich atmosphere of propane gas at an elevated temperature (mostly 930°C) in a fluidized bed furnace. This process created a material consisting of a high-carbon steel case and a low-carbon steel core.

The influences of carbon gradient and carbon level on tensile strength, micro-hardness, ductility, and work-hardening rate were investigated for two Fe-Mn grades: Fe-24Mn and Fe-30Mn. In this work, the use of HCl prior to carburizing was found to provide a more consistent carbon concentration gradient at the surface. This method was subsequently applied in all carburizing treatments. The carburized Fe-24Mn steel exhibited austenite at the surface and epsilon (ε)-martensite at the core. For the carburized Fe-30Mn steel, the structure was austenitic at the surface and the core.

In general, the mechanical test results indicate that the strength of both steels is increased and the ductility decreased after carburizing. Carburizing for shorter times (5 to 30 minutes) provided optimal mechanical properties.
For the Fe-30Mn austenitic samples, the strength and ductility were insensitive to the carbon gradient. What matters is the total carbon level. This means the steel can be manufactured with low levels of carbon, which facilitates cold rolling, and potentially forming. Carbon can then be added in a final carburizing treatment to achieve the desired properties.

Higher yield strengths were seen in the Fe-24Mn samples after carburizing, compared to samples with the same carbon content distributed evenly over the sample thickness. This is due to the hard martensitic core. The yield strength of these steels can be described by a law of mixtures relation.

‘Up-hill’ diffusion of carbon was seen in manganese depleted surface layers and this is attributed to increased carbon activity coefficients in these regions.

Finally, the study also showed the potential of two-stage carburizing and cold rolling to obtain attractive strength-ductility trade-offs in carburized Fe-24Mn steel, which has a hard ε-martensite core with a soft austenite surface.
# List of Symbols and Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>TWIP</td>
<td>Twinning Induced Plasticity</td>
</tr>
<tr>
<td>HMS</td>
<td>High Manganese Steel</td>
</tr>
<tr>
<td>TRIP</td>
<td>Transformation Induced Plasticity</td>
</tr>
<tr>
<td>IF</td>
<td>Interstitial Free</td>
</tr>
<tr>
<td>BH</td>
<td>Bake-Hardening</td>
</tr>
<tr>
<td>HSLA</td>
<td>High Strength Low Alloy</td>
</tr>
<tr>
<td>DP</td>
<td>Dual Phase</td>
</tr>
<tr>
<td>PM</td>
<td>Powder Metallurgy</td>
</tr>
<tr>
<td>AHSS</td>
<td>Advanced High Strength Steel</td>
</tr>
<tr>
<td>fcc</td>
<td>Face-centered cubic</td>
</tr>
<tr>
<td>ε-martensite</td>
<td>Epsilon martensite</td>
</tr>
<tr>
<td>γ</td>
<td>Austenite</td>
</tr>
<tr>
<td>d</td>
<td>Grain size</td>
</tr>
<tr>
<td>OM</td>
<td>Optical Microscope</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SEM-EDX</td>
<td>Scanning Electron Microscopy-Energy Dispersive X-ray</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>GDOES</td>
<td>Glow Discharge Optical Emission Spectroscopy</td>
</tr>
<tr>
<td>n</td>
<td>Work-hardening exponent</td>
</tr>
<tr>
<td>dσ/dε</td>
<td>Work-hardening rate</td>
</tr>
<tr>
<td>γ→ε</td>
<td>Austenite to martensite phase transformation</td>
</tr>
<tr>
<td>SFE</td>
<td>Stacking Fault Energy</td>
</tr>
<tr>
<td>α’</td>
<td>Excess interaction coefficient between solutes</td>
</tr>
<tr>
<td>σ</td>
<td>True stress</td>
</tr>
<tr>
<td>ε</td>
<td>True strain</td>
</tr>
<tr>
<td>t₁, t₂, t₃</td>
<td>Carburizing times</td>
</tr>
<tr>
<td>J</td>
<td>Carbon flux</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
</tr>
<tr>
<td>β</td>
<td>Mass transfer coefficient</td>
</tr>
<tr>
<td>D</td>
<td>Carbon diffusion coefficient</td>
</tr>
<tr>
<td>C_p</td>
<td>Carbon potential</td>
</tr>
<tr>
<td>C_s</td>
<td>Carbon at the surface</td>
</tr>
<tr>
<td>C_x</td>
<td>Carbon at x depth below the surface</td>
</tr>
<tr>
<td>C_o</td>
<td>Initial carbon content</td>
</tr>
<tr>
<td>x</td>
<td>Depth below the surface</td>
</tr>
<tr>
<td>X_D</td>
<td>Case depth</td>
</tr>
<tr>
<td>φ</td>
<td>Concentration in mol/m³</td>
</tr>
<tr>
<td>t</td>
<td>Diffusion time</td>
</tr>
<tr>
<td>C(x, t)</td>
<td>Carbon concentration below the surface at a given time</td>
</tr>
<tr>
<td>erf</td>
<td>Error function</td>
</tr>
<tr>
<td>D_o</td>
<td>Maximum diffusion coefficient</td>
</tr>
<tr>
<td>Q_d</td>
<td>Activation energy for diffusion</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>R</td>
<td>Gas constant</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrogen Chloride</td>
</tr>
<tr>
<td>Cu-Kα</td>
<td>Monochromatic copper K alpha radiation</td>
</tr>
<tr>
<td>SDAS</td>
<td>Secondary Dendrite Arm Spacing</td>
</tr>
<tr>
<td>wt %</td>
<td>Weight percent</td>
</tr>
<tr>
<td>ε-Fe</td>
<td>Iron martensite</td>
</tr>
<tr>
<td>γ-Fe</td>
<td>Iron austenite</td>
</tr>
<tr>
<td>P = 2t_s/t</td>
<td>Proportion of surface layer</td>
</tr>
<tr>
<td>σ_s</td>
<td>Yield stress of the carburized surface layer</td>
</tr>
<tr>
<td>σ_c</td>
<td>Yield stress of the core</td>
</tr>
<tr>
<td>t</td>
<td>Thickness of sample</td>
</tr>
<tr>
<td>t_s</td>
<td>Thickness of the carburized layer</td>
</tr>
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Chapter 1: Introduction

1.1 Overview

The development of high strength steel is of considerable interest to the automotive industry, which demands excellent mechanical properties. Recently, in response to this, composition changes and process variations of Hadfield Fe-Mn steel have been made [1, 2]. These steels, called Twinning Induced Plasticity (TWIP) steels, are characterized by a high work-hardening capacity that allows tensile strengths above 1000 MPa to be obtained with exceptional ductility (total elongation 50 to 60%) [3, 4]. A comparison of the mechanical properties between high manganese steels and other conventional steels is displayed in Figure 1.1.

Figure 1.1. Comparison of strength and ductility between high manganese steel (HMS) Transformation Induced Plasticity (TRIP), TWIP and other types of steels, interstitial free (IF), bake-hardening (BH), high strength low alloy (HSLA), dual phase (DP) and powder metallurgy (PM) [5-8].
Two important examples of TWIP steels are the Fe-Mn-C [2, 3, 9] and Fe-Mn-Al-Si [2, 7, 10, 11] steels. They are both variations on the traditional Hadfield steel, which is used in wear impact applications such as in oil drilling, mining, railways, and construction [12-14].

The newer steels were introduced for processing into sheet products whereas Hadfield steels are most commonly used in the as-cast state [12, 15]. The hot and cold rolling used to manufacture sheet require a base level of formability. The modern TWIP steels display, in general, good formability but in cold rolling and sheet forming, very high loads can be encountered particularly during cold rolling. High loads pose challenges for mill operation, tooling wear and dimensional control [1, 6, 16-19].

In the present work, the prospect of introducing carbon in a carburizing treatment is explored as a means of opening up the processing window of TWIP steels. The addition of carbon towards the end of the sheet production route will allow prior forming steps to be carried out under lower loads.

The current work also examines the potential of carburizing to control and possibly improve the mechanical properties. The role of carbon in high manganese steels can be seen in Figures 1.2 and 1.3 for: i) a Fe-24Mn steel, which comprises a mixture of face-centered cubic (fcc) austenite, \( \gamma \), and hexagonal epsilon martensite, \( \varepsilon \); and ii) a Fe-30Mn steel, comprising a stable austenitic structure.

The Fe-24Mn material displays a lower yield strength and increase in ductility when carbon is added. The present work explores the potential to use this effect at the surface to increase the ductility. The addition of carbon to the Fe-30Mn steel grade increases strength and work-hardening. Without carbon, the material is expected to display superior cold rollability [20]. The addition of carbon in a carburizing treatment following cold rolling has the potential to restore strength and work-hardening to the final annealed sheet.
Figure 1.2. Stress-strain curves of the Fe-24Mn and Fe-24Mn-0.4C steels [21, 22]. Failure strains are shown.

Figure 1.3. Stress-strain curves of the Fe-30Mn and Fe-30Mn-0.5C steels [20]. Failure strains are shown.
The making, shaping and treating of steel evolved to provide better quality high manganese steel for automotive application. Over the years, the developments of high manganese steels have led to many steel compositions with a great variety of microstructure and performance [7, 23, 24].

The interest in TWIP steels in automotive industry began when the two main steel suppliers (Arcelor and ThyssenKrupp) started to develop a new family of manganese steel [25]. This steel has a possibility of light weight vehicle construction, crash resistant and increase passengers’ safety [24-26]. Ferrando et al. [25] reported that the TWIP steels can reach a deformation of 35% for a resistance of 1400 MPa and have exceptional capacity to absorb crash energy.

The use of TWIP steel for the actual press forming of automotive shock absorber housing proved the excellent in practice of this steel [27]. Kim et al. [28] proposed a TWIP steel composition which shifts the intense twinning to room temperature. This steel was used as a high performance steel for stamping of thin strip for automotive application.

Cooman et al. [27] noted that the interest in TWIP steels from the automotive industry renewed the interest in their properties. Mainly, three types of TWIP steel compositions have been investigated: Fe-22Mn-0.6C [9], Fe-18Mn-0.6C, Fe-18Mn-0.6C-1.5Al [29] and Fe-Mn-Si-Al containing low carbon [30].
1.2 Aim and Scope of Work

The main aim of the present work is to determine and understand the potential of carburizing to improve the processing and performance of TWIP steels. Two sub-aims are identified: i) to develop a method of carburizing by which high manganese steels can accept carbon during carburizing; ii) to determine and understand the impact of a carbon gradient on the mechanical properties.

In order to provide understanding of the effect of carburizing on TWIP steels, two high manganese steels are examined: Fe-24Mn and Fe-30Mn. These are subjected to hot and cold rolling followed by carburizing. These steels were chosen so that prior to carburizing one (Fe-24Mn) is predominantly ε-martensite and other (Fe-30Mn) is predominantly austenite. The materials are carburized for varying carburizing times to achieve differing carbon gradients. The resulting structure and mechanical properties are characterized.

The observed carbon gradients and surface carbide formation in these steels are examined and characterized. A law of mixtures is employed to describe the mechanical performance of different carbon gradients. Finally, the study examines how carburizing can be best exploited for improved production and performance of sheet metal TWIP steels.

1.3 Thesis Outline

The work reviewed is organized into seven chapters that describe the state of the art on TWIP steels and the work conducted to study this type of steels when subjected to carburizing cycles. The introduction of the thesis, Chapter 1, summarizes the importance of these materials, set out the objective
and aims of the work and describes the way into which the work carried out will be dealt with.

Chapter 2 comprises an overview of the literature concerning Hadfield steel and TWIP steel. The manufacturing processes such as casting, rolling, carburizing and annealing of high manganese steels are reviewed. This section also provides information on TWIP steel composition and its mechanical properties. The principles of carburizing are discussed. The literature relating to the effects of carbon, surface carbide formation and heat treatment on the microstructure evolution and mechanical properties is also discussed.

Chapter 3 describes the alloying compositions and experimental procedures. The manufacturing processes (casting, rolling, annealing) for the Fe-24Mn and Fe-30Mn steels are presented. The preparation of the samples for carburizing, mechanical testing and microstructure analysis using the optical microscope (OM), Scanning Electron Microscopy-Energy Dispersive X-ray spectroscopy (SEM-EDX), X-Ray Diffraction (XRD), Glow Discharge Optical Emission Spectroscopy (GDOES) are described. Different methods of carburizing using a fluidized bed furnace in order to obtain the optimum strength and ductility are presented.

Chapter 4 characterizes the microstructures. The effects of manufacturing processes and carbon gradient on the microstructure are examined. Chapter 5 reports and discusses mechanical properties. The relationship between the carbon gradient, heat treatment and mechanical properties of TWIP steels are analyzed using law of mixtures. The effects of carburizing time on yield strength, ultimate tensile strength, work-hardening rate, reduction in area, uniform elongation and total elongation of these steels are presented. The results are explained in terms of the microstructure.

Chapter 6 explores the possibility for optimization of the manufacture of Fe-24Mn and Fe-30Mn steels. Two-stage carburizing and cold rolling are examined.
Chapter 7 contains the overall conclusion of this research and suggestions for future work.
Chapter 2: Literature Review

2.1 Development of High Manganese Steels

This chapter reviews and summarizes previous studies on the microstructure and mechanical properties of high manganese steels. Much work has been conducted on these steels and many compositions have been examined [2, 9, 20, 21, 31-36]. Work by Bouaziz and Guelton [37], Niendorf et al. [38], Mi et al. [39], Hua et al. [40], Bracke et al. [41], and Zhenli et al. [42] showed that TWIP steel maintains an austenite structure during deformation and that high work-hardening arises because of mechanical twinning.

Modelling is used to predict the characteristics of the microstructure. After the invention of Hadfield steel, studies by Shun et al. [43] and Renard et al. [44] aimed to understand the extraordinary work-hardening behaviour. Bouaziz and Guelton [37] and Spindola et al. [45] developed models of TWIP effect on work-hardening. From the model, Spindola et al. [45] found that the work-hardening exponent, n, could attain values as high as 0.6 in TWIP steels. Previous work by Liang et al. [21], Lee and Kim [46] and Curtze [47] reported that the n-value of other Fe-Mn steels (24, 26 and 30 wt % manganese) was between 0.38 to 0.40.

Modelling of the TWIP effect by Allain et al. [48] showed that the increase in volume fraction of twins decrease the mean free path of dislocations. Their work also showed that the resulting high work-hardening rate delayed necking during tensile testing. They also conclude that the work-hardening effect is due to mechanical twinning. Their model is in agreement with the results produced from the experimental work by other workers [37, 44, 45, 49-51].
The mechanical properties of TRIP and TWIP are reviewed. The high rate of strain hardening allows higher tensile strengths and higher uniform elongations. TRIP steels show a high yield strength (450 to 550 MPa) and a high ultimate tensile strength (800 MPa) but the elongation is usually lower (23 to 30%) compared to TWIP steels [29, 40]. Work by Cooman et al. [27] made a comparison of stress-strain curves and strain hardening rates of hot rolled TRIP and TWIP steel grades (Figure 2.1). This figure clearly shows the high work-hardening of TWIP compared to TRIP steel.

![Figure 2.1. Comparison of the true stress and strain hardening rate of TRIP and TWIP steels as a function of true strain [27, 52].](image)

The high manganese steels are of interest for new demand of automotive industry [Grajcar, 2008]. In the last few years, the design of Fe-Mn-C TWIP type steels has been refined by: Bouaziz et al. [2], Allain et al. [9], Wang et al. [20], Liang et al. [21], Lu et al. [22], Shun et al. [43], Rezende et al. [53], Remy and Pineau [54], Nakano et al. [55] and Scott et al. [56] who introduced modifications in manganese and carbon contents. Scott et al. [56], Cooman et al. [6] and Funatani [57] focused on the design and
manufacturing of TWIP steels for superior forming and crashing performance. The basis of the compositional variations examined in these studies is outlined in the next section.

2.2 Composition

2.2.1 Hadfield Steel

Sir Robert Hadfield reported on high manganese steel in 1883. His steel had a high strength and high work-hardening capacity with a reasonable ductility [13]. These properties made it useful for abrasion and heavy impact applications. Hadfield steels are still used in rock crushers and railway tracks due to their excellent wear resistance and high work-hardening capability [13, 58-61]. The major alloying components in Hadfield steel are 10 – 14 wt % manganese and 1.0 – 1.4 wt % carbon [13].

The mechanical properties of Hadfield steel are dependent on the carbon and manganese content. The tensile strength and ductility of this steel reaches a maximum at 1.2 wt % of carbon content [62]. In the literature, mechanical properties of Hadfield steel are reported as: yield strength, 380 MPa; ultimate tensile strength, 970 MPa; uniform elongation, 50%; hardness, as-quenched, 190 HB; hardness, at fracture, 500 HB, and rapid work-hardening [13, 50].

Bayraktar et al. [62] showed that the unusually high strain hardening of Hadfield steel can be attributed to the formation of twins that provide strong barriers to dislocation motion. Low SFE and high concentration of interstitial atoms also have pronounced effects on the yielding and strain hardening of this material. The low SFE promotes the formation of deformation twins [63]. Hadfield steels were found to have an austenitic structure and a low SFE of 23 mJ/m$^2$ (13Mn-1.2C) [63, 64].
2.2.2 Twinning Induced Plasticity (TWIP) Steels

TWIP steels contain manganese levels between 15 and 28 wt % [2, 9, 31, 39]. Hua et al. [40] and Grassel et al. [30] stated that the TWIP effect is dominant when the manganese content is higher than 25% [40]. They found that there was no phase transformation in TWIP steel during cooling or deformation, but that mechanical twinning dominates [65]. Two important high manganese TWIP steel classes are: i) Fe-Mn-Al-Si and ii) Fe-Mn-C.

Dini et al. [10], Grassel et al. [30], and others [66, 67] investigated the effects of aluminium and silicon on the mechanical properties of high manganese steels. Both aluminium and silicon provide improved mechanical properties at a higher strain rate [30]. The purpose of aluminium addition was to increase the SFE and suppress the austenite-martensite ($\gamma \rightarrow \varepsilon$) transformation. Silicon increased the SFE for small quantities and decreased it at higher contents (over 4 wt %) [68, 69]. With the addition of these elements, low carbon levels can be tolerated.

Extensive research has been reported on high manganese TWIP steels with slightly different compositions [6]. Frommeyer et al. [30] investigated the effect of manganese content in Fe-Mn-Al-Si steel. Their results revealed that this steel exhibited a decrease in UTS (930 to 610 MPa), but an increase in total elongation (46 to 88%) with increasing a manganese content.

The other important class of TWIP steels, the Fe-Mn-C grades, have been heavily studied [2, 3, 9, 21, 32]. The work by Kato et al. [70] showed that carbon increases the yield strength and lattice parameter of austenitic Fe-Mn alloys. This is in agreement with the results reported by Lu et al. [22]. Tian and Zhang [71] showed that carbon lowers the $\varepsilon$-martensite start temperature of the Fe-Mn system.

Compositions of Fe-Mn-C steels studied by previous researchers (and their field of interest) are summarized in Table 2.1. From the table, it can be
seen that the focus of research has been in various areas such as carbide precipitation, work-hardening, effect of grain size, deformation twinning and transformation of $\varepsilon$-martensite. A range of manganese (20 to 30 wt %) and carbon (0.1 to 1.2 wt %) contents have been examined. Cooman et al. [6] noted that recent interest had focused on Fe-18Mn-0.6C and Fe-22Mn-0.6C steels. Previous work [9, 32, 72] showed that these steel were characterized by a high work-hardening rate which resulted in a combination of higher strength and uniform elongation.

Table 2.1. Key studies relating to Fe-Mn-C TWIP steels.

<table>
<thead>
<tr>
<th>Steel Composition</th>
<th>Aims of the Published Work</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>20Mn-1.0C</td>
<td>Hot rolling</td>
<td>[29]</td>
</tr>
<tr>
<td></td>
<td>Carbide precipitation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Work-hardening</td>
<td></td>
</tr>
<tr>
<td>22Mn-0.6C</td>
<td>Hot and cold rolling</td>
<td>[9, 31, 32, 36, 73]</td>
</tr>
<tr>
<td></td>
<td>TWIP effect</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Strength-ductility</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\gamma$-$\varepsilon$ transformation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Carbine formation</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Work-hardening</td>
<td></td>
</tr>
<tr>
<td>22Mn-0.2C/0.4C/0.6C/1.2C</td>
<td>Cold rolling</td>
<td>[2, 74]</td>
</tr>
<tr>
<td></td>
<td>Strength-ductility</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Effect of grain size</td>
<td></td>
</tr>
<tr>
<td>23Mn-0.54C</td>
<td>Hot and cold rolling</td>
<td>[34]</td>
</tr>
<tr>
<td></td>
<td>Strength-ductility</td>
<td></td>
</tr>
<tr>
<td>24Mn-0.25C</td>
<td>Hot rolling</td>
<td>[75]</td>
</tr>
<tr>
<td></td>
<td>Effect of tensile temperature</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Strength-ductility</td>
<td></td>
</tr>
<tr>
<td>24Mn-0.12C</td>
<td>Hot rolling</td>
<td>[76]</td>
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<td></td>
<td>Deformation twin and $\varepsilon$-martensite</td>
<td></td>
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<tr>
<td>25Mn-0.14C</td>
<td>Hot rolling</td>
<td>[66]</td>
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<td></td>
<td>Strength-ductility</td>
<td></td>
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<tr>
<td></td>
<td>Work-hardening</td>
<td></td>
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<tr>
<td>25Mn-0.26C</td>
<td>Cold rolling</td>
<td>[77]</td>
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<td></td>
<td>$\varepsilon$-martensite transformation</td>
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<td></td>
<td>Strength-ductility</td>
<td></td>
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<tr>
<td>26Mn-0.2C</td>
<td>Annealing</td>
<td>[54]</td>
</tr>
<tr>
<td></td>
<td>Effect of $\gamma$-$\varepsilon$ phase transformation</td>
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<td>Effect of tensile temperature and strain rate</td>
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<td></td>
<td>Strength-ductility</td>
<td></td>
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<tr>
<td>29Mn-0.8C</td>
<td>Cold rolling</td>
<td>[2]</td>
</tr>
<tr>
<td></td>
<td>Effect of grain size</td>
<td></td>
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<td></td>
<td>Strength-ductility</td>
<td></td>
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<tr>
<td>30Mn-0.5C</td>
<td>Hot and cold rolling</td>
<td>[20, 21]</td>
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<td></td>
<td>Effect of strain rate and temperature</td>
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<td>Strength-ductility</td>
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<td>Work-hardening</td>
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Hua et al. [40] compared TRIP and TWIP effects. Their results showed that the TRIP effect was present in the Fe-Mn-C steels when the manganese content was lower than 20 wt %, while the TWIP effect was dominant when the manganese content was higher than 25 wt %. The roles of carbon and manganese in these steels are strongly related to the stacking fault energy (SFE) [55].

Stacking faults are formed when the regular atomic stacking sequences are disturbed [78]. The energy of stacking faults in high manganese steels is strongly dependent on chemical composition and temperature [72, 73, 79]. Increasing manganese between 15 and 28 wt % increases the SFE and so too does an increase in carbon level [72, 73].

Mechanical twinning is favoured for SFE values between 18 and 25 mJ/m$^2$ [32, 41, 73] and at lower temperatures [3, 9]. Twinning is the favoured deformation mode at low values of SFE because the faults in the lattice are wider and dislocation cross-slip is more difficult [80]. Dislocation glide is the dominant deformation mechanism when the SFE is high (60 mJ/m$^2$) [81].

Chun et al. [82] reported that $\varepsilon$-martensite can be formed during cooling or by deformation of austenite when the stacking fault energy is low. As reported by Mazancova and Mazanec [81] and Nakano and Jacques [55], lowering the manganese and carbon content led to a $\varepsilon$-martensite structure in high manganese steel due to the low SFE. Rohatgi et al. [83] reported that high manganese steels undergo strain induced $\varepsilon$-martensite phase transformation at relatively low SFE, (~18 mJ/m$^2$). A model correlating the SFE with composition and plasticity mechanisms was proposed by Allain et al. [9]. Their results are shown in Figure 2.2. The iso-SFE lines follow Schumann’s lines (solid line in Figure 2.2), which is in agreement with an activation of the $\varepsilon$-martensite transformation controlled by the SFE values. The increase in SFE with manganese and carbon was also reported in references [84] and [85].
Figure 2.2. Calculated iso-SFE lines in the manganese-carbon map at 300K. The SFE value is dependent on manganese and carbon content. The solid lines proposed by Schumann [86] describe the boundary of mechanical and thermal martensite transformation [9].

Scott et al. [56] studied the relationship between SFE, tensile properties and deformation temperatures of high manganese steels between 77 and 673K. They suggested that the low uniform elongation and tensile strength which occurred at temperatures between 500 and 673K was due to dislocation gliding (SFE is 80 mJ/m²). They noted that a high uniform elongation which occurred at room temperature was caused by mechanical twinning (SFE is 20 mJ/m² and strain hardening exponent is higher than 0.40). Their work also showed that the highest ultimate tensile strength occurred at low temperatures with a lower total elongation because of the decrease in SFE.
2.3 TWIP Steel: Microstructures

2.3.1 Phases in High Manganese Steels

Bracke et al. [87] reported a phase composition for the Fe-Mn binary system (Figure 2.3). Austenite and $\alpha'$-martensite are the phases present at room temperature for up to 15 wt % manganese. The microstructure consists of $\varepsilon$-martensite and austenite for manganese composition ranging between 15 and 27 wt % (Figure 2.3) [88]. These results also suggested that steel with a manganese content exceeding 28 wt % was fully austenitic and does not undergo $\varepsilon$-martensite transformation. This finding is in agreement with the results of work by Sato et al. [89].

![Figure 2.3. Phase composition for the Fe-Mn binary systems [87, 88].](image)

The effects of manganese and carbon on the phase transformation in a ternary Fe-Mn-C system at 298K after quenching and tensile testing are presented in Figures 2.4 and 2.5, respectively. Figure 2.4 shows the effect of manganese and carbon on the equilibrium phase at room temperature. It can be seen that an increase in manganese and carbon stabilize the austenite. Two concurrent deformations are considered in Figure 2.5; mechanical twinning...
and/or martensite formation. Intense mechanical twinning (shaded area) is observed after deformation with manganese levels of 15 to 30 wt % and carbon contents of 0.4 to 0.9 wt %.

Figure 2.4. Phase diagram of the Fe-Mn-C system after quenching at 298K [56].

Figure 2.5. Distribution of phases and occurrence of twinning in the Fe-Mn-C system after tensile testing at 298K [56].
2.3.2 Precipitation of Carbide

Cooman et al. [27] used carbon (approximately 0.6 mass %) in an alloy containing less than 25 mass % of manganese to obtain a stable room temperature austenite phase. Higher carbon additions result in formation of $M_3C$ carbide (Figure 2.6) [27, 90-92]. Furthermore, carbide precipitates decrease the concentration of carbon in solution and result in a decrease of the SFE [93]. Iker et al. [94] found that lowering the SFE by carbide precipitation makes twinning start earlier.

![Figure 2.6](image_url)  
Figure 2.6. Effect of carbon and manganese on Fe-Mn-C equilibrium phase diagram. The shaded area refers to the superposition of the 700°C austenite stability range and the microstructure observed after quenching to room temperature from 950°C [27].

According to Samarin et al. [95], the reduction of the tensile strength of high manganese steel was caused by the formation of $\varepsilon$-martensite when the carbon content is 1.15 wt %. For a higher carbon level (1.30%), they found that the tensile strength of this steel decreased due to precipitation of carbide...
during deformation. Both of these compositions of carbon led to a deterioration in the mechanical properties of the TWIP steels.

In summary, SFE affects deformation twinning and the formation of ε-martensite. The value of SFE is dependent on the manganese and carbon content. At low SFE and temperatures, (but not so low as to form ε-martensite) deformation twinning is dominant, resulting in high work-hardening, high strength and high ductility. Carbon precipitates out as iron and manganese carbide at high carbon levels. This resulted in a decrease in the strength and toughness of the steel.

2.3.3 Examples of the Effect of Manganese on Microstructure

Work by Liang et al. [21] and Silman [96] showed that the microstructure of annealed Fe-24Mn steel consists of austenite and ε-martensite. Example structures from their work are given in Figure 2.7a. For higher manganese levels, between 29 and 31 wt %, steel remained fully austenitic after quenching in water [54, 97, 98]. This also agrees with work by Curtze and Kuokkala [90]. The microstructure of annealed Fe-30Mn steel had a uniform equiaxed austenite grain and annealing twins were observed (Figure 2.7b) [21, 87].

![Figure 2.7. Scanning electron microstructure of annealed Fe-Mn steels: a) Fe-24Mn – austenite and ε-martensite, and b) Fe-30Mn – austenite [21].](image-url)
The recent review by Bouaziz et al. [2] and work by Liang et al. [21] demonstrated that the microstructure of deformed Fe-25Mn steel at room temperature shows the extensive presence of mechanical twins (Figure 2.8). This result is consistent with the work of Allain et al. [32], who found that the volume fraction of twins deformed at room temperature increased with strain. Bouaziz et al. [2] reported that Fe-30Mn steel deformed at room temperature consists of dislocation cells (Figure 2.9) and no significant mechanical twinning was observed. This is also in good agreement with the work by Cooman et al. [27].

![Figure 2.8. Evolution of microstructures of TWIP steels (Fe-22Mn-0.6C) at room temperature and different strain level: a) un-strained, b) 18%, c) 26% and d) 34% [32, 96].](image-url)
The volume fraction of $\varepsilon$-martensite for high manganese steel was determined at various cooling and deformation temperatures by Liang et al. [21], Kim et al. [85], Jun et al. [99] and Lee et al. [46]. Jun and Choi [99] reported that the volume fraction of $\varepsilon$-martensite in these alloys increased with decreasing manganese content (23 to 17 wt %) and cooling temperature (25 to -196°C) (Figure 2.10). Lee et al. [46] and Popov [100] also reported that manganese decreases the $\varepsilon$-martensite start temperature. Finally, the volume fraction of $\varepsilon$-martensite in the Fe-26Mn steel increased from 22 to 40% after tensile testing at room temperature, compared to 60% at 77K as reported by Lee and Kim [46].
Figure 2.10. Volume fraction of \( \varepsilon \)-martensite as a function of cooling temperature of high manganese steels \[99\].

### 2.3.4 Examples of the Effect of Carbon on Microstructure

Curtze and Kuokkala \[90\] and Cooman et al. \[6\] noted that the optimum properties in high manganese steels was achieved by stabilizing the austenite at room temperature. This was done by adding carbon into the Fe-Mn steel for a manganese content less than 27 wt %. Scott et al. \[56\] also noted the limits on the percentage of carbon in the Fe-Mn steel composition. They worked with carbon compositions between 0.4 wt % (sufficient carbon for solid solution hardening) and 0.9 wt % (formation of carbide).

Remy and Pineau \[54\] and Tomota et al. \[97\] reported that for manganese contents ranging from 22 to 25 wt %, the volume fraction of \( \varepsilon \)-martensite in these steels was found to be approximately 45% after quenching in water. Georgieva et al. \[101\] and Volosevich et al. \[102\] noted that the addition of carbon (0.2%) stabilized the austenite in Fe-24Mn steel by increasing the SFE. This result is consistent with the volume fraction of \( \varepsilon \)-martensite reported by Lu et al. \[22\] (Figure 2.11).
They also reported that the carbon is the most effective element among manganese, aluminium, chromium to reduce $\varepsilon$-martensite start temperature of Fe-Mn steels [103].

Bouaziz et al. [2] also reported that the carbon content in high manganese steels triggers twinning and possibly other dislocation mechanism. However, the increase in SFE with increasing carbon content would suppress twinning by preventing the dissociation of dislocations, thereby stabilizing the austenitic structure.

Ono et al. [104] noted that high carbon concentration in TWIP steels lead to the precipitation of iron carbide. They also found that any carbon tied up in precipitates decreases the concentration in solid solution and results in lower SFE.

Work by [105] showed that the work-hardening depends strongly on the carbon content for Fe-Mn-C TWIP steels (with similar SFE). This is consistent with the TEM analysis by [106] revealed stronger twins due to solution hardening in TWIP steel hardened by carbon.

A review of the microstructure-property of high manganese steels by Bouaziz et al. [2] concluded that carbon contents higher than 1.2 wt % has a detrimental effect on the toughness and ductility due to the formation of cementite precipitation in austenite.

Fracture analysis of Fe-Mn-C steel containing higher carbon content (0.6 wt % carbon) by Eileen [74] revealed a highly necked region and led to an overall ductile failure. The steel demonstrated brittle failure with low post-uniform elongation when the carbon level was 0.2 wt %. According to Eileen [74], the damage mechanism was void nucleation and growth at $\gamma - \varepsilon$ boundaries and interface with $\varepsilon$-martensite containing high dislocation density.
Figure 2.11. Volume fraction of martensite as a function of carbon in Fe-24Mn steel [22].

2.4 Mechanical Properties

2.4.1 Effect of Twinning Induced Plasticity (TWIP) in High Manganese Steels

The tensile properties of TWIP steels are dependent on manganese and carbon levels, deformation temperature and strain rate [72, 85]. Typical true stress-true strain curves of TWIP steels tested at room temperature until fracture are presented in Figure 2.12 [2]. Bayraktar et al. [62] found that carbon addition improved strength and ductility. However, when carbon was increased to above 1.2%, it led to a decrease in ductility. Many researchers found that the increase of carbon content to 0.6% (with 25 wt % manganese) raises tensile strength to about 1000 MPa [2, 3, 12, 21, 45, 79, 107, 108].

The levels of manganese and carbon in TWIP steel affect its stress-strain curves (Figure 2.12). It can be seen that the Fe-24Mn steel has a higher flow stress than Fe-30Mn steel. The addition of 0.5 wt % carbon into
Fe-30Mn steel increases its flow stress by ~150 MPa. The highest flow stress is observed in the steels with low manganese level (12 and 17 wt %) and high carbon content (1.2 and 0.95 wt %).

Previous studies by Renard and Jacques [49] showed that high manganese steel exhibited high strength and elongation before necking due to the TWIP effect during straining. Allain et al. [48] stated that this results from the increase in volume fraction of twinning with strain. Work by Bouaziz et al. [3], Renard and Jacques [49], Tsakiris and Edmond [109] and Holm [110] also noted that high manganese steels had a higher total elongation (up to 80%) when the concentration of manganese and carbon were in the range of 17 to 22 wt % and 0.4 to 0.8 wt %, respectively.

![Stress-strain curves of various TWIP steels](image)

Figure 2.12. Stress-strain curves of various TWIP steels tensile tested at room temperature [2, 21, 51, 62, 105] with coarse grains between 20 and 40 µm.
Liang et al. [21] found that Fe-24Mn steel had a higher flow stress than Fe-30Mn steel (grain size ranges between 20 and 50 μm) with similar elongation after deformation at room temperature. This was caused by the stress-induced austenite to ε-martensite transformation. Their results were compared to the work by Wang et al. [20] for the Fe-30Mn steel containing 0.5 wt % carbon (grain size is 17 μm). The latter steel showed much higher flow stress and elongation compared to Fe-24Mn and Fe-30Mn steels without carbon. The increase in tensile properties of the Fe-30Mn-0.5C steel was reported to be due to the TWIP effect during deformation at room temperature.

Recently, Chin et al. [111] studied the deformation mechanisms of two TWIP grades, Fe-22Mn-0.6C and Fe-18Mn-0.6C-1.2Al. They found that Fe-22Mn-0.6C had a higher strain hardening and that this resulted in a high tensile strength and elongation of this steel. This is in agreement with the finding by Allain et al. [32] who reported that a high strain hardening effect due to mechanical twinning resulted in a high elongation to fracture (70%), high tensile strength (1200 MPa) and high work-hardening. The importance of SFE, twinning and high work-hardening rates has been studied by many workers [37, 49, 112].

In regard to manufacturing, Scott et al. [56] carried out deep drawing and cold stamping for a structural automotive part of TWIP steel (Fe-22Mn-0.6C). They suggested that the TWIP effect enabled high manganese steel to withstand cold working.
2.4.2 Effect of Manganese on the Mechanical Properties of Fe-Mn Alloys

2.4.2.1 Strength and Ductility

Kutz [113] stated that manganese had a role in strengthening steel although in Hadfield steels, manganese has little effect on yield strength. Peters [114] noted that maximum tensile strengths of Hadfield steel can be attained with 12 to 13 wt % manganese content [114]. In the other case, Charles and Berghezan [75] and Sato et al. [75, 89] demonstrated that a high manganese content (> 28 wt %) gave an austenitic structure characterized by a low yield strength (132 MPa) with high ductility at room temperature. This result is consistent with the work by Hua et al. [40]. They concluded that solid solution strengthening is not a major strengthening mechanism, but that strain-induced phase transformation or twinning makes a very important contribution to the strength of these steels [75, 115, 116].

In this section, tensile data from published work is compared to understand the effect of manganese in these steels. The yield strength and ultimate tensile strength of binary Fe-Mn steel as a function of manganese content are presented in Figures 2.13 and 2.14, respectively. (The grain size is different for these various grades but the main trends can still be observed). The most notable feature of the yield and tensile strength data is a step change at approximately 27 wt % of manganese. As discussed previously, steel with a manganese content over 27 wt % is fully austenite [21]. Lower manganese grades are characterized by structures containing significant amounts of $\varepsilon$-martensite [21, 40].

Manganese content in the range from 20 to 24 wt % results in the formation of $\varepsilon$-martensite, which has a high yield strength and ultimate tensile strength at room temperature. For a higher manganese contents (> 30 wt %), austenite is observed and this is characterized by a low yield strength.
Figure 2.13. Yield strength of binary Fe-Mn steels as a function of manganese content.

Figure 2.14. Ultimate tensile strength of binary Fe-Mn steels as a function of manganese content.
The effect of manganese on the total elongation of the Fe-Mn steels is demonstrated in Figure 2.15. In the range of 20 to 36 wt %, total elongation values show little sensitivity to manganese levels. It is true, however, that the highest elongations appear at the highest manganese level.

Figure 2.15. Total elongation of binary Fe-Mn steels as a function of manganese content.

Liang et al. [21] examined the change of volume fraction of \(\varepsilon\)-martensite with true strain in Fe-24Mn and Fe-30Mn steels at room temperature and at cryogenic temperature (77K) by using XRD. They found that increasing the true strain caused the amount of \(\varepsilon\)-martensite in both steels to increase. At lower temperature, the volume fraction of \(\varepsilon\)-martensite in Fe-24Mn steel was found to be higher than at 293K. The volume fraction of \(\varepsilon\)-martensite in Fe-30Mn steel was consistently much lower than that in Fe-24Mn steel for a given strain (Figure 2.16).
2.4.2.2 Effect of Carbon on Mechanical Properties

Bouaziz et al. [2] reported that the mechanical properties of Hadfield steel can be modified further by adding carbon (from 1.2 to 1.4 wt %). According to Bayraktar et al. [62] this steel showed a decrease in ductility when the carbon content was greater than 1.2 wt %. It was found that a higher carbon content (> 1.4 wt %) resulted in precipitation of carbides, and decreases both strength and ductility were reported by Gulyaev et al. [60]. This is in agreement with the work by Balogun et al. [117].

Lu et al. [22] investigated the effect of carbon on the mechanical properties of the Fe-24Mn steel. Their results revealed that a small addition of carbon reduced the ε-martensite start temperature of this material and enhanced the tensile ductility. They also found a significant decrease in yield strength with a small increase in carbon content (0.01 to 0.2 wt %). This was
caused by a decreasing volume fraction of $\varepsilon$-martensite. The yield strength of this steel increased when Lu et al. [22] changed the carbon content from 0.2 to 0.4 wt %.

Figure 2.17 displays the influence of carbon on yield strength of Fe-Mn-C steels with different compositions of manganese and carbon. The values in the plot were obtained from the published stress-strain curves of various Fe-Mn-C steel grades. It can be seen that the yield strength of Fe-Mn steels (20 to 26 wt % manganese) without carbon vary from 370 to 450 MPa after tensile testing at room temperature. These samples exhibited a mixed austenite and $\varepsilon$-martensite structure. At the same level of manganese (e.g. 24 wt %), the yield strength shows a decrease with a small increase in carbon content (from 0.1 to 0.2 wt %). However, a consistent increase in yield strength is observed for higher concentrations of carbon.

Figure 2.17. Effects of carbon on yield strength of a various Fe-Mn-C steels.
Typical values of ultimate tensile strength for the Fe-Mn-C steels, measured in previous research are given in Figure 2.18. These steels showed an increase in ultimate tensile strength with increasing carbon content (regardless of the content of manganese). Wang et al. [20] noted that a higher ultimate tensile strength in these steels was caused by the presence of the mechanical twinning. The greatest ultimate tensile strength was revealed by the steels containing carbon higher than 1.0 wt %, due to formation of carbide [118].

![Figure 2.18](image-url)

Figure 2.18. Effects of carbon on ultimate tensile strength of a various Fe-Mn-C steels.
The total elongations of the Fe-Mn-C steels with different carbon content are scattered between values of 0.3 and 0.6% (Figure 2.19). Most total elongations of these steels increased with carbon content up to 0.6 wt %. Lower total elongation was observed when the carbon content was greater than ~0.6 wt %. This is possibly due to the precipitation of carbide at the grain boundary [2, 94, 104]. Iker et al. [94] suggested that the loss in ductility was due to the coalescence of cavities at the carbide-matrix interfaces in TWIP steels.

![Figure 2.19. Effects of carbon on total elongation of various Fe-Mn-C steels.](image-url)
2.5 Manufacturing Processes Issues in TWIP Steels

Manufacturing of high manganese steel is of interest to many steel producers (e.g. Kobe Steel, Posco, ThyssenKrupp Stahl, Arcelor Mittal) [2]. A good combination of strength and elongation characteristics must be achieved to meet the specific needs of the automotive industry. TWIP steels under consideration today are capable of being produced by casting followed by hot and cold rolling.

The production of the steel plate commences with the continuous casting of molten steel into a slab. The cast slabs are usually reheated and the oxide scale removed before rough rolling. The plate is then passed through a finishing mill, where it is rolled to ~2 – 4 mm in thickness. In the last step, hot rolled strip is cooled and coiled into a coil [119]. The hot rolled plate can be processed into several types of intermediate product according to their applications (Figure 2.20): slitting; shearing; pickling; and galvanizing [120-122].
Figure 2.20. The overview of manufacturing process flow of hot and cold rolled steel plate [120, 123].
2.5.1 Rolling High Manganese Steel

Rolling and forming, was noted by Dobrzanski et al. [91] to be the most challenging stage of TWIP steel manufacture. Here, the flow stress-strain behaviour of this steel has to be well understood in relation to deformation temperatures and loads. Work by Colin and Philippe [124] showed that the problem with cold rolling high manganese Fe-Mn based steels at higher total reductions is that of surface cracking. For Hadfield steel, J. Zhijie et al. [125] found that at a higher cold rolling force, the strip shape was difficult to control due to high work-hardening. This finding is in good agreement with the work of Mcewan [118] who noted that the work-hardening of these steels pose challenges for some forming operation. Other groups [56, 118] suggested that Hadfield steel had a low formability, due to a large amount of brittle carbide (> 1.0 wt % carbon), which made it difficult to roll into a thin sheet.

Colin and Philippe [124] observed that cracking in cold rolling can be avoided by continuous annealing which enables a better combination of strength-ductility steel for subsequent processing. An important processing variable in TWIP steel production is the annealing temperature. Mi et al. [39] and Kang et al. [126] investigated the effects of annealing on cold rolled manganese steels and found that the elongation was significantly increased from 10 to 65% at temperature ranges from 550 to 1100°C. Work by Mcewan [118] also showed that a series of cold rolling steps with intermediate heating and quenching were required to produce a final thickness of steel sheet. This adds considerable cost to the process.

Samek and Arenholz [23] found that TWIP steel required a higher hot rolling force than that of rolling other steels (plain carbon, low alloy and dual phase). They discussed both hot and cold rolling of high manganese steels. They also suggested that a higher rolling force was required in cold rolling of TWIP steels which contained ε-martensite structure. Work by Hamada and his group [66], found that high manganese and aluminium in TWIP steel
(Fe-Mn-Al-Si) resulted in a significant increase in hot deformation resistance as compared to that of low carbon steels.

2.5.2 Sheet Metal Forming

The manufacturing processes of hot and cold rolled sheet often involve sheet metal forming; such as bending, punching deep drawing, and trimming [127]. Many ductile and light materials (e.g. aluminium and magnesium) and high strength steels (e.g. DP, TRIP and TWIP) are used in sheet metal forming. TWIP steels exhibit a large springback after forming and this result in final assembly problems [128-130]. Springback occurs as an elastic unloading behaviour when sheet metal parts are released from forming tools [129]. It is more severe for higher strength steels [131].

2.6 Principles of Carburizing

Carburizing is a surface hardening process where carbon is added into the steel surface at temperatures between 850 and 950°C [132-135]. This process involves the interstitial diffusion of carbon [136] and is used in many applications to increase the surface and strength of components such as sleeves, shafts, bearings and gears [132, 137-140].

After carburizing, the highest concentration of carbon is at the surface and the carbon level drops towards the core of parts (e.g. [141]). To understand carburizing, schematic diagrams of a non-steady state of concentration of carbon in the steel for various carburizing times are illustrated in Figures 2.21a to c. Carburizing can be divided into two stages: Stage 1 - carbon enrichment stage, which refers to a carbon transfer from the furnace to the steel, and; Stage 2 - diffusion stage, which refers to carbon diffuses into the steel [142].
Figure 2.21. Concentration of carbon profile of low carbon steel at varying times \((t_1 < t_2 < t_3)\): a) \(t_1\), b) \(t_2\) and c) \(t_3\). \(C_s\) is a carbon concentration at the surface; \(C_o\) is an initial carbon content; \(t_1\), \(t_2\) and \(t_3\) are carburizing times. Stage 1 is a carbon enrichment stage and Stage 2 is a diffusion stage [142].

Smith [143] stated that the case depth of concentration of carbon below the steel surface is dependent on carburizing time and temperature. They found that at elevated temperature the rate of carbon deposited on the surface is greater than the diffusion rate. This results in uneven distribution of carbon and leads to surface carbide formation.

The carburizing reaction at the furnace-steel interface and the diffusion of carbon in the steel was also explained by Cavaliere et al. [144]. This group reported that carbon potential on the surface was dependent on the temperature and the pressure. It remained constant during the treatment and at the same time the carbon diffused in the bulk. In this way the concentration profile from the surface to the core changed with the treatment time.

Karabelchtchikova [145] explained that carbon concentration at the surface arises by the reaction of carburizing gases at the furnace-steel interface. A schematic diagram of carbon transfer and the key parameters in this process is shown in Figure 2.22. The mass transfer coefficient \((\beta)\) defines the flux of carbon atoms \((J)\) from the atmosphere to the steel surface and the
coefficient of carbon diffusion in the steel $(D)$ describes carbon diffusion into the austenite.

Figure 2.22. Boundary conditions for non-steady state diffusion [136]. $J$ is a carbon flux, $\beta$ is a mass transfer coefficient, $D$ is a carbon diffusion coefficient, $C_p$ is a carbon potential, $C_s$ is carbon at the surface, $C_x$ is carbon at $x$ depth below the surface, $C_o$ is the initial carbon content in the steel and $x$ is the distance below the surface.

A carburizing atmosphere is typically composed of a mixture of carbon monoxide, hydrogen, nitrogen, carbon dioxide, water vapour and a hydrocarbon gas for carburizing such as methane, propane and/or butane [145, 146]. In the present work, propane and nitrogen gases were used. Carburizing reactions specific to the atmosphere are as follows:

$$C_3H_8 \rightarrow C + 2CH_4$$

Equation 2-1
Carburizing was further complemented by thermal dissociation of the methane formed during carbon precipitation:

\[ CH_4 \rightarrow C_{Fe} + 2H_2 \]  

Equation 2-2

### 2.6.1 Kinetics of Carburizing

Case depth of carburizing can be defined as the depth from the surface to an arbitrarily defined ‘end’ of the diffusion zone. The case depth of carbon concentration below the carburizing steel surface can be estimated using the following equation:

\[ Case\ depth, \quad X_D \sim \sqrt{2Dt} \]  

Equation 2-3

where \( X_D \) is the case depth below the surface in m, \( t \) is the diffusion time in s, and \( D \) is the carbon diffusion coefficient in m²/s [145, 147, 148].

The carburizing temperature, time, and carbon concentration affect the diffusion rate of carbon in the steel [57, 132, 149]. The relationship between these parameters can be expressed by Fick’s Second Law [149]. The rate of the concentration change is equal to the decrease of the diffusion flux and the equation is given as [147]:

\[ \frac{\partial c (x,t)}{\partial t} = \frac{\partial}{\partial x} \left[ D \left( \frac{\partial c(x,t)}{\partial x} \right) \right] / \partial t \]  

Equation 2-4
For a concentration independent diffusion coefficient, $D$, Equation 2-4 is simplified to:

$$\frac{\partial c (x, t)}{\partial t} = D \left[ \frac{\partial^2 c(x, t)}{\partial x^2} \right]$$ \hspace{1cm} \text{Equation 2-5}

or,

$$\frac{\partial \phi}{\partial t} = D \frac{\partial^2 \phi}{\partial x^2}$$ \hspace{1cm} \text{Equation 2-6}

where $\phi$ is the concentration in mol/m$^3$, $t$ is the diffusion time in s, $D$ is the diffusion coefficient in m$^2$/s and $x$ is the depth below the surface of the sample in m.

According to Goldstein and Moren [150], for non-steady state diffusion, concentration of carbon in the steel as a function of both depth and time can be written as follows, by assuming infinite sample thickness and constant surface carbon concentration:

$$\frac{C(x, t) - C_o}{C_s - C_o} = 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$ \hspace{1cm} \text{Equation 2-7}

where $C (x, t)$ is the carbon concentration in wt % below the surface, $x$ in m at a given time, $t$ in s, $C_s$ is the surface carbon concentration in wt %, $C_o$ is the initial carbon concentration in wt %, $D$ is the diffusion coefficient of carbon in m$^2$/s, $x$ is the depth below the surface of the sample in m and erf is the error function.
The relationship between diffusion coefficient and temperature is given by the Arrhenius equation as follows [151]:

\[ D = D_0 \exp\left(-\frac{Q}{RT}\right) \]  

Equation 2-8

where, \( D \) is the carbon diffusion coefficient in m\(^2\)/s, \( D_0 \) is the maximum diffusion coefficient in m\(^2\)/s, \( Q_d \) is the activation energy for diffusion in J/mol, \( T \) is the temperature in Kelvin and \( R \) is the gas constant in J/mol K.

This expression is insensitive to composition but, according to Karabelchtchikova [145], the coefficient of carbon diffusion in austenite is influenced by the concentration of carbon in the steel [57, 110, 136, 152].

2.6.2 Carburizing of Steels

The early work on carburizing steel carried out by Chernov et al. [153], Malinov et al. [107], Pumpyanskaya et al. [154], Reynoldson [155] and Mayer [156] showed considerable improvement in strength and hardness properties. Carburizing can also produce better performance steel with a high strength case and a tough core as reported in later work by Oyetunji and Adeosun [157], Karabelchtchikova [145], Palaniradja et al. [132], Jacquet et al. [158], Karaman and Ackan [159], and Turpin et al. [142].

Thibaux et al. [152] have carburized Fe-Mn-C with a low manganese content (1.5 wt %). Their results showed three stages in the concentration of carbon profiles (Figure 2.23). They explained that the ‘up-hill’ diffusion in Stage I and the carbon peak in Stage II in terms of the segregation of manganese during cooling. This steel showed a consistent diffusion of carbon
in Stage III during carburizing. It also can be seen that the surface carbon content is not constant with carburizing times.

Figure 2.23. Carbon profiles of the carburized Fe-1.5Mn-0.13C steel at 900°C [152, 160].

In a steel containing 4% manganese, Nestor et al. [161] found very high carbon saturation (3.6 wt % at 968°C) at the surface. This was verified by the presence of massive carbides in the microstructure. Their results also showed that the microstructures of both surface and core were martensitic after cooling.

A two-stage caburization technique was used by Dragomir and Druga [162, 163] using a fluid bed furnace. In the first stage, the carbon potential was held over the soot limit and in the second stage, the diffusion took place. This method enabled prevention of carbon precipitation.
2.6.3 Effect of High Manganese and Carbon on Diffusion Coefficient in Steels

Above it was noted that the diffusion coefficient of carbon in steel is composition dependent. In this section, the effect of manganese and carbon on the diffusion coefficient is reviewed. Lee [164], Reger et al. [165], Tsuguyasu et al. [166], Darken [167], Wells and Mehl [168] and Kulka et al. [169] investigated the effects of manganese on carbon diffusion in austenitic steel. They also investigated the effect of carbon in relation to the manganese diffusion coefficient. The work of Wells and Mehl [168] showed that the diffusion coefficient of manganese increased with increasing manganese content and that increasing the carbon increases the diffusion rate of manganese. They also stated that increasing the carbon content from 0.02 to 1.25 wt % raised the diffusion of manganese from approximately 10 to 40 x 10^{-11} \text{cm}^2/\text{s}.

It is claimed that manganese decreases the activity of carbon and this affects the carbon diffusion [170]. The diffusion coefficients of segregated elements (e.g. manganese) are much smaller than of carbon (the difference is 4 orders of magnitude). This means that practically only carbon will diffuse during carburizing [171].

Andersson et al. [172] and Huang [172, 173] made calculations performed by Thermo-Calc software and by other thermodynamic models [166, 174] concerning the interaction between manganese and carbon in iron to prove that manganese decreases the activity of carbon in the austenite. Manganese enhances the diffusion when the steel has a great difference in manganese content between the segregated and non-segregated areas during homogenization [171].
Reger et al. [165] proved that carbon activity was influenced by the distribution of alloying elements using diffusional calculations. This is in agreement with Majid and Child [175] and Lakhtin [176] who reported that diffusion in the steel is dependent on the chemical composition. Reger et al. [165] and Salak and Selecka [177] explained that manganese decreased the activity of carbon and affects its diffusivity. This result supports the finding by Darken [167].

Previous work by Kral et al. [178] and Kulka et al. [169] and Reger et al. [171] found that manganese decreased the activity of carbon and thus affects carbon diffusion in steel. The carbon follows the redistribution of manganese and this can cause the diffusion of carbon to go ‘up-hill’.

Carbon activity in the Fe-Mn-C system was studied by Kulka et al. [169] by controlling the carburizing atmosphere at 1173 K. Their results displayed that carbon activity was diminished by manganese. This is in agreement with the work by Wada et al. [166] who stated that a higher manganese content decreased the activity coefficient of carbon.

2.7 Opportunity

The present review has shown that carbon is essential for favourable mechanical properties in high manganese TWIP steels. It is also seen that TWIP steels present challenges to steel processing due to high rolling forces. In some cases, cracks occur during cold rolling of steel into sheet.

The idea is to add carbon through carburizing after the part has been produced. This would permit the prior rolling to be carried out under lower rolling loads and this in-turn is expected to give better product quality.
The microstructure of carburized high manganese steels is expected to consist of an austenite surface and a $\varepsilon$-martensite or austenite core, depending on manganese level. This microstructure may display unique favourable properties. Carburizing also provides an opportunity to modify the properties of these steels directly from the furnace.

The carburizing of high manganese steels has hardly been studied, so this opportunity presents a number of manufacturing challenges. The effect of a carbon gradient on the mechanical response of Fe-Mn-C TWIP steels is also unknown.
Chapter 3: Methodology

3.1 Introduction

The experiments carried out in this work can be divided into two: 1) preliminary work; and 2) main work. The preliminary work was undertaken to investigate the feasibility of carburizing high manganese steels. In this work, hot rolled Fe-24Mn steel plates with low carbon content were carburized. In the main work, the Fe-24Mn and Fe-30Mn steels were hot and cold rolled before carburizing.

This section commences with the manufacturing processes used in the study. It then outlines the characterization techniques employed.

3.2 Casting and Homogenization

Two TWIP steel grades (Fe-24Mn and Fe-30Mn) were prepared by argon shielded induction melting in a 25 kg capacity casting furnace (Figure 3.1). A small quantity of aluminium was mixed with the molten metal during melting in order to reduce the formation of oxides of iron and manganese (deoxidation). Both Fe-24Mn and Fe-30Mn steels were melted at 1550°C and poured into a steel mould (200 mm x 80 mm x 40 mm) to make 10 kg cast ingots. The melts were then allowed to solidify in the mould. Finally, the mould was opened after cooling for 2 hours and the casts were taken out.
A sample 20 mm x 20 mm x 15 mm in size was cut from each ingot and analyzed for the chemical composition using a Spectrometer. The rough surfaces of as-cast material were removed by a milling machine. The chemical compositions of the two steels used for this study are given in Table 3.1. The steels with 24 and 30 wt % manganese will be referred to from now on as Fe-24Mn and Fe-30Mn steels.

Table 3.1. The composition of as-cast high manganese steels used in this work.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>Fe-24Mn</td>
<td>Balance</td>
</tr>
<tr>
<td>Fe-30Mn</td>
<td>Balance</td>
</tr>
</tbody>
</table>
The steel bars were cut from the ingot to approximately 50 mm x 60 mm x 15 mm in size and ultrasonically cleaned in organic solvent for 15 minutes before being loaded into a vacuum furnace at vacuum level of $9 \times 10^{-5}$ Torr (Figure 3.2). The homogenization was performed by heating as-cast steel bars to 1180°C at 400°C/h and soaked at 1180°C for 10 hours. The bars were slow cooled to room temperature in the furnace.

Figure 3.2. Homogenization of as-cast Fe-24Mn and Fe-30Mn steels in a vacuum furnace.

### 3.3 Hot Rolling

The homogenized Fe-24Mn and Fe-30Mn steels were prepared for hot rolling (Figure 3.3) by heating in a Muffle Furnace at 1100°C for 30 minutes. A thermocouple (2 mm in diameter) was inserted into drilled holes on the steel surface for temperature measurement. The steel bars were hot rolled in four passes to a plate 4 mm thick. The total rolling reduction was 73%. The hot rolling was performed for all steel bars in the same rolling direction.
Table 3.2 shows the parameters of hot rolling for the Fe-24Mn and Fe-30Mn steels for each pass. The temperature ranged from 1000 to 1050°C to overcome heat loss during rolling. The final hot rolled plates were air cooled to room temperature.

Table 3.2. The parameters of hot rolling Fe-24Mn and Fe-30Mn steels.

<table>
<thead>
<tr>
<th>No. of passes</th>
<th>Sample thickness (mm)</th>
<th>Reduction/pass (%)</th>
<th>Rolling temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.0</td>
<td>30</td>
<td>1000-1050</td>
</tr>
<tr>
<td></td>
<td>(starting thickness)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10.5</td>
<td>30</td>
<td>1000-1050</td>
</tr>
<tr>
<td>3</td>
<td>7.4</td>
<td>30</td>
<td>1000-1050</td>
</tr>
<tr>
<td>4</td>
<td>5.2</td>
<td>23</td>
<td>1000-1050</td>
</tr>
<tr>
<td></td>
<td>4.0</td>
<td>-</td>
<td>Air cooled</td>
</tr>
<tr>
<td></td>
<td>(final thickness)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Hot rolling created a large layer of scale on the surface of both steels. The removal of this scale was the main difficulty encountered during the preparation of the samples. Sand blasting was used to clean the surface before cold rolling.

### 3.4 Cold Rolling and Annealing

Cold rolling was carried out to produce a better surface finish and to generate an accurate thickness for both Fe-24Mn and Fe-30Mn steel plates. The hot rolled steel plates were cold rolled to 1.5 mm in thickness and in the same direction used for hot rolling. The cold rolling was done without reversing the rolling direction and a lubricant was applied on the rollers. The cold rolling was carried out in three stages using a laboratory rolling mill equipped with a roll diameter of 200 mm (Figure 3.4).

![Cold rolling mill](image-url)
The first stage of cold rolling involved the reduction of plate from 4.0 to 2.6 mm. In the second and third stages, reduction was to 2.0 and 1.5 mm, respectively. The reduction per pass was 0.1 mm for each stage (to ensure uniform thickness and to minimize the shear strain in the plate), corresponding to approximately 63% thickness of total reduction. After cold rolling, at each stage, plates were annealed in a fluid bed furnace at 1000°C for 30 minutes under a nitrogen atmosphere. These parameters were chosen in order to avoid warping and distortion of steel plates. The purpose of annealing at this stage is to remove the various stress and strain developed during cold rolling. Otherwise cracks may occur due to non-uniform stress distribution.

Details of cold rolling and annealing parameters are given in Table 3.3. The heat was turned off and the plates were taken out of the furnace at 800°C (under a nitrogen atmosphere). Finally, steel plates were air-cooled to room temperature.

Table 3.3. The parameters of cold rolling Fe-24Mn and Fe-30Mn steels. Annealing was performed for steel samples after cold rolling to 2.6 mm, 2.0 mm and 1.5 mm thick.

<table>
<thead>
<tr>
<th>Rolling stage</th>
<th>Thickness (mm)</th>
<th>Reduction/pass (mm)</th>
<th>No. of Passes</th>
<th>Heat treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.0 – 2.6</td>
<td>0.1</td>
<td>14</td>
<td>Annealing at 1000°C for 30 minutes for each stage</td>
</tr>
<tr>
<td>2</td>
<td>2.6 – 2.0</td>
<td>0.1</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.0 – 1.5</td>
<td>0.1</td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>
3.5 Carburizing

Carburizing of Fe-24Mn and Fe-30Mn steels was performed in a fluidized bed furnace at 930°C. Various carburizing times were used: 5, 15, 30, 60 and 120 minutes. Before carburizing, precautions were taken to ensure that the furnace had a low carbon and oxygen content in order to prevent surface contamination (oxidation) and inconsistent carbon concentration. This involved the oxidation of soot on the retort walls and on the alumina powder bed by heating in air to 930°C.

Next, a nitrogen gas environment was introduced for 60 minutes to purge oxygen out of the furnace, prevent surface oxidation during carburizing. The nitrogen was then enriched by 15% propane (C₃H₈) gas to provide a carburizing atmosphere. After carburizing, propane gas was turned off, but the nitrogen flow was maintained for 5 minutes. The samples were rapidly quenched in water at room temperature and held there for 10 minutes.

In the present work, carburizing can be summarized into three stages (Figure 3.5): 1) heating at temperature of 930°C; 2) carbon mass transfer and diffusion at varying times, and; 3) quenching in water to retain the as-carburized composition and structure.

![Figure 3.5. Heat treatment cycle for carburizing Fe-24Mn and Fe-30Mn steels.](image)
Fe-24Mn and Fe-30Mn steel samples to be carburized were cut from 1.5 mm thick cold rolled plates. The samples for carbon analysis (25 mm x 25 mm x 1.5 mm) and tensile testing (70 mm x 15 mm x 1.5 mm) were cut to size. The tensile samples were then machined into tensile gauges using a CNC machine (25 mm x 5 mm x 1.5 mm). Next, samples were ground with a 600 μm grit paper to remove the oxide layer and provide a better surface finish for carburizing.

Three samples for carbon analysis and microstructure characterization and five samples for tensile testing were prepared for each carburizing condition. The Fe-24Mn and Fe-30Mn steel samples which were not to be carburized were also prepared for comparison. All samples for carbon analysis and tensile testing were hung in a steel basket using small diameter steel wire (Figure 3.6). The basket was placed into the furnace for carburizing, after which the samples were quenched in water.

Figure 3.6. Samples for carbon analysis and tensile testing hung in a steel basket prior to carburizing.
In the present work, two carburizing procedures were carried out: one without hydrogen chloride (HCl) pre-treatment, and one with HCl pre-treatment.

3.5.1 Carburizing without HCl Pre-treatment

In this process, the Fe-24Mn and Fe-30Mn steel samples were carburized without the activation of HCl gas. The carbon atmosphere in the furnace was enriched by 15% propane and nitrogen gases with flow rates of 0.26 and 1.22 m$^3$/h, respectively. The samples were then carburized at 930°C for 5, 15, 30, 60 and 120 minutes and finally quenched in water.

In this experiment, the effects of surface oxide formation (e.g. iron or manganese oxide) on carburizing Fe-24Mn and Fe-30Mn steels were also investigated. Five samples of these steels were each heat treated in a Muffle furnace under atmospheric condition at 1000°C for 60 minutes in order to produce a different concentration of oxygen at the surface. These samples were then carburized at 930°C for 30 minutes without HCl pre-treatment. One group of the samples was not heated, but rather ground with grinding paper (600 µm). Ethanol was poured on the samples to prevent surface oxide formation during grinding. All ground samples were stored under ethanol before carburizing. Then, the effects of oxide layer on carburizing Fe-24Mn and Fe-30Mn steels were characterized. The depth of the oxygen concentration below the surface of these steels was measured using GDOES. Finally, their microstructures were examined using an optical microscope.
3.5.2 Carburizing with HCl Pre-treatment

The carburizing here involves an activation of HCl gas at 10 vol % for 10 minutes, followed by carburization at 930°C. This method was proposed to ensure the uniformity and predictability of carbon concentration at the surface. The mixture of propane and nitrogen gases was applied with the same flow rate as that used in the carburizing without HCl pre-treatment (0.26 and 1.22 m³/h). Then, the samples were carburized for 5, 15, 30, 60 and 120 minutes.

Carburizing was made to go faster by including HCl-containing activating compound fed to the carburizing furnace. Activation of HCl was done in the same furnace as carburization without removing the samples. The samples were treated (deoxidation) by contact with HCl before carburizing gas was activated. The activation of HCl can achieve a substantial increase in the amount of carbon concentration performed under a set of carburizing conditions. This, in turn, means including HCl gas being fed to the furnace significantly enhances the rate of the overall carburization.

The carburized steel samples were then characterized for the carbon gradient, microstructure, and mechanical properties. The samples were weighed before and after carburizing to determine the amount of carbon diffusion. The samples were also characterized in terms of carbon concentration at the surface, weight gain and micro-hardness.

3.5.3 Annealing after Carburizing

Annealing was performed in order to investigate the effect of a uniform carbon level on the microstructure and mechanical properties (strength and ductility) of the carburized Fe-24Mn and Fe-30Mn steels. All carburized samples were annealed at 1000°C for 30 minutes under a nitrogen atmosphere in a fluid bed furnace. These samples were cooled in the furnace
to 800°C under nitrogen and then were air cooled to room temperature. The annealing is required to relief the residual stresses developed in hot and cold rolling. Instead annealing was performed to restore the ductility of these steels.

### 3.6 Surface Compositions

Quantitative depth profiles of carbon, manganese, oxygen and iron in the surface region of the carburized TWIP steels were attained by a LECO GDS-750A (Figure 3.7). Glow Discharge Optical Emission Spectrometer (GDOES) set at a constant discharge of 700 V and 20 mA.

![Quantitative depth profiles analysis of the steel sample using Glow Discharge Optical Emission Spectrometer (GDOES).](image)

The quantitative depth profiling limit is 80 – 100 μm. To construct a profile of a carburized region of depth (> 100 μm), the following procedure was determined. First, the sample was cleaned with ethanol and then held
under vacuum (0.11 Torr) in the workplace chamber. The minimum sample size was 10 mm x 10 mm in order to ensure it was held securely at the vacuum chuck and also to avoid leakage of nitrogen and argon gases during the analysis. Successive layers of the surface were sputtered (Figure 3.8a). A sputtered crater from an initial analysis performed to the maximum profile depth was removed by grinding with a 1200 μm grit paper for subsequent sputters (Figure 3.8b). The successive depth profiles were combined to construct a profile to approximately 500 μm below the surface. The GDOES profile presented a concentration of carbon in weight percent as a function of depth.

![Figure 3.8.](image1)

(a) Sputtered crater on the surface after GDOES, and (b) removed crater by grinding with an abrasive paper (1200 μm grit).

3.7 Carbon Level (Carburizing and Annealing Fe-24Mn and Fe-30Mn Steels)

In order to measure the effect of carbon levels on the microstructure and mechanical properties of this steel steels, carburized and annealed steel samples were used. The annealing treatment was carried out as mentioned in 3.5.3. The concentration of carbon immediately below the surface and at approximately 750 μm (half of a samples’ thickness) below the surface were measured using GDOES. The concentration profile was also acquired for manganese content.
3.8 Metallography

The Fe-24Mn and Fe-30Mn steel samples were prepared by mechanical polishing and chemical etching. The samples were cut from the carburized steel plate and sectioned using a Struers Accutom-50 grinding cutter. The samples were then hot mounted and fixed in a 30 mm diameter ring mould with 15 ml conductive Polyfast resin using a Struers CitoPress-20. The heating temperatures were set at 80°C (pre-heating) and 180°C for 3 minutes of each temperature. The hot mounted samples were then cooled by water for 2 minutes.

Three grades of silicon carbide (SiC) abrasive paper (240, 600, and 1200 μm grit) were used for rough grinding of hot mounting samples. Next, cloths with three grades of particle size (9, 3, and 1 μm) were used for fine polishing using a Struers RotoPol-21 for 10 minutes with a load of 30 N against the cloth. A few drops of lubricant were applied onto the pad as a suspension for smooth polishing. After that, the samples were ultrasonically cleaned for 15 minutes in an organic solvent prior to the next polishing with a finer particle size of cloth. For the purpose of metallography, well polished samples were etched in 3% nital solution for 15 seconds to make the boundaries visible. The samples were thoroughly rinsed with ethanol and then immediately dried for 30 seconds at temperature 100°C using a heater. Finally, the microstructures of the carburized Fe-24Mn and Fe-30Mn steels were examined using an Olympus DP-70 optical microscope and scanning electron microscope. The same procedures were applied in preparing the samples for micro-hardness testing and SEM-EDX.

3.9 Micro-hardness

Micro-hardness of hot rolled and cold rolled plate before and after annealing was measured using the Micro-hardness Tester FM-700. A diamond
indenter with an applied load of 1000 g for 15 seconds was used to measure the micro-hardness of uncarburized and carburized Fe-24Mn and Fe-30Mn steel samples.

Five indentations in the cross section of the samples were performed at different locations but at the same depth. The distance between two micro-hardness indentations at the same depth was 200 μm. The micro-hardness measurement was repeated every 200 μm down until the opposite edges was reached. The samples for micro-hardness testing were prepared using the same methods as mentioned in Section 3.8.

3.10 Tensile Testing

Tensile samples with a gauge section of 1.5 mm in thickness, 5 mm in width, and 25 mm in length for both steels were prepared using a CNC Triac-Fanuc ATC milling machine. Tensile tests were carried out at room temperature with a strain rate of $10^{-3}$ s$^{-1}$ using a 30 kN Instron 5567 machine. The strain of the tensile samples was measured using an MTS extensometer. The non-contacting extensometer was attached to measure the deflection of the sample in comparison to the deflection of the load frame. The samples were gripped using a wedge-action grip, which increased the squeezing pressure applied to the sample.

For each carburizing time, five steel samples which were carburized without HCl and with HCl pre-treatment prior to carburizing were tensile tested. The carburized steel samples which were annealed at 1000°C for 30 minutes had also been tested at the same temperature and strain rate. The yield strength, ultimate tensile strength, uniform elongation, total elongation and reduction in area of all those samples were then plotted for comparison.
3.11 SEM-EDX Mapping and Spot Scanning

The distribution of manganese in the homogenized, cold rolled and annealed Fe-24Mn and Fe-30Mn steels were examined using a Leica 440 Scanning Electron Microscope (SEM) equipped with an Energy-Dispersive X-ray spectrooscope (EDX). At this stage, an EDX-mapping was utilized to analyze the selected surface layers of these steels. The steel samples mounted in Polyfast resin were ground and polished before etching. First, steel samples were properly loaded into the vacuum chamber. The beam and probe current were 15 kV and 2.0 nA, respectively. The EDX detector was engaged and the working distance between the electron beam and steel samples in the vacuum chamber was 25 mm. The ISIS software was loaded for the EDX-mapping of 500 x 300 \( \mu \text{m}^2 \) in area at a magnification of 150X. The plot of the chemical concentration in these steels was produced after the scanning was completed.

For spot scanning, the same steel samples and SEM procedures were used, as mentioned above for mapping. In this experiment, the ‘spot scanning’ option was selected. Data from spot scanning were acquired over depth intervals of 50 \( \mu \text{m} \) from the surface (as in Figure 3.9). The spot scanning was repeated for three times at same level of depth. The manganese and carbon compositions for each level were recorded.
3.12 X-Ray Diffraction (XRD)

X-Ray Diffraction (XRD) analysis was performed to identify the phases and chemical compositions of the constituents of the Fe-24Mn and Fe-30Mn steels using a X’Pert Pro PANalytical X-Ray Diffraction machine. This process was carried out using monochromatic Cu-K$_\alpha$ radiation at 40 kV and 50 mA. A rotating-head anode diffractometer was used to scan the angular $2\theta$ ranged of 40 - 100$^\circ$ with a scanning speed of 0.5$^\circ$/min. The plot of the intensity of the beam against the diffraction angle gives a series of peaks. In this experiment, steel samples were cut from the uncarburized and carburized steel plates to 15 mm × 15 mm × 1.5 mm in size for the analysis. The phase change during manufacturing and heat treatment of as-cast Fe-24Mn and Fe-30Mn was also examined using XRD. The formation of $\varepsilon$-martensite and austenite for both carburized Fe-24Mn and Fe-30Mn steels were determined.
by the direct comparison method using the integrated intensities peaks of 
\( \varepsilon \)-martensite and austenite. The phase identification of these steels was also 
measured using the X-Pert High Score Plus software. The phase compositions 
in as-cast, cold rolled and carburized Fe-24Mn and Fe-30Mn steel samples 
were identified using the same software. The chemical compounds presented 
at the peak of XRD pattern were matched and compared to a large database of XRD patterns found in the particular software.
Chapter 4: Microstructure

This chapter reports on the microstructure characterization of the Fe-24Mn and Fe-30Mn steels which were carburized for various times ranging from 5 to 120 minutes. The process-structure relationship of these steels is discussed.

4.1 Introduction

The aim of this chapter is to analyze the effect of carbon on the evolution of microstructure of the carburized high manganese steel. In the carburizing without HCl pre-treatment, the Fe-24Mn steel samples were successfully carburized to obtain austenite (soft phase) at the surface and \( \varepsilon \)-martensite (hard phase) at the core. In order to overcome inconsistencies in carbon profiles, the subsequent work performs carburizing with HCl pre-treatment. However, further investigation was carried out to clarify the effect of the oxide layer on the carbon diffusion during carburizing.

The preliminary work showed that the carburized layer is easily detected due to etching and stabilization of austenite. The microstructure of the Fe-24Mn steel carburized at 930°C for 30 minutes in a 15% of propane gas is shown in Figure 4.1. Two layers are observed: a carbon rich austenite layer at the surface and a \( \varepsilon \)-martensite dominated layer at the core. The results of X-Ray diffraction reveal that the \( \alpha' \)-martensite is not observed in the carburized Fe-24Mn sample. The carbon rich layer is readily observed in this steel sample because carburizing stabilizes the austenite phase by lowering the \( \varepsilon \)-martensite start temperature. Thus, in the initial experiments on Fe-24Mn steel, carbon was successfully introduced into the samples. With this encouragement a more extensive study was commenced, using Fe-24Mn and Fe-30Mn steels.
Figure 4.1. Optical microstructure (20X magnification) of the Fe-24Mn steel carburized at 930°C for 30 minutes without annealing. The sample was etched in 3% nital solution.

4.2 Characterization before Carburizing

4.2.1 Microstructure

In this section, microstructures of as-cast, annealed and rolled Fe-24Mn and Fe-30Mn steels are presented. The optical micrographs of the primary and secondary dendrite structure of as-cast for both steels are shown in Figures 4.2a and b, respectively. The secondary dendrite arm spacing (SDAS) for the Fe-24Mn and Fe-30Mn steels was calculated using Image-J software and the average spacings are approximately 17 and 30 μm, respectively. Both steel samples were homogenized at 1000°C for 10 hours with the same cooling rate. The different in the SDAS of the samples is also dependent on the manganese content which is related to the SFE. This result is in good agreement with Ferraiuolo et al. [179] who stated that the SFE changed from 24 to 45 mJ/m² with increasing manganese level. This is also supported by Chao et al. [180] who observed the similar micrographs (as Figure 4.2).
Figure 4.2. Optical micrographs (10X magnification) of as-cast Fe-24Mn and Fe-30Mn steels. The samples were etched in a 3% nital solution for 15 seconds.

The microstructures of both steels after annealing (1000°C, 10 hours, 9 x 10⁻⁵ Torr), and slow cooling in a vacuum furnace are shown in Figure 4.3. Plate-like epsilon (ε) martensite structure was observed in Fe-24Mn steel as depicted in Figure 4.3a. The Fe-30Mn steel consisted of a uniform equiaxed austenite with a grain size of 170 μm (Figure 4.3b). Dendrite ‘shadows’ are evident in this image. These are likely to be regions of manganese segregation.

Figure 4.3. Optical microstructures (20X magnification) of homogenized Fe-24Mn and Fe-30Mn steels. The samples were etched in a 3% nital solution for 15 seconds.
The microstructures of the cold rolled Fe-24Mn steel (62.5% reduction) and annealed, which is composed predominately of ε-martensite are shown in Figure 4.4a. The Fe-30Mn steel structure looks similar in Figure 4.4b. The result shows that bands are clearly observed in these microstructures. This is probably due to the segregation of manganese during solidification and rolling. The effect of banding is more marked in Fe-24Mn steel as it is likely these features are elongated versions of the ‘shadows’ seen in Figure 4.3a. This is in agreement with Caballero et al. [181] who stated that the manganese is most responsible for the development of microstructure banding. Work by Wang et al. [20] confirmed by TEM that Fe-30Mn steel has an austenite consisting of dislocation cell structures and manganese bands after cold rolling.

![Fe-24Mn and Fe-30Mn microstructures](image)

Figure 4.4. Optical microstructures (10X magnification) of the cold rolled (62.5% reduction) and annealed (1000°C, 30 minutes) Fe-24Mn and Fe-30Mn steels. The samples were etched in a 3% nital solution for 15 seconds. The thickness of the samples is 1.5 mm.
4.3 Characterization after Carburizing without HCl

Pre-treatment

4.3.1 Microstructure

Microstructure characterization was performed to evaluate the depth of the carburized layer under the surface of the cold rolled Fe-24Mn and Fe-30Mn steel samples. The optical microstructures of these carburized steels for a range of carburizing times are shown in Figures 4.5 and 4.6. It can be seen that the depth of the carburized layer below the surface varies as a function of carburizing time. The depth of the layers was measured to be between 200 and 600 µm for 5 to 120 minutes carburizing times, respectively. The ε-martensite structure of the Fe-24Mn steel has been replaced by austenite at the surface. However, ε-martensite dominates in the core (Figure 4.5). In contrast, austenite is present throughout the thickness of the Fe-30Mn steel (Figure 4.6). In this grade, etching is clearly sensitive to carbon level so the carburized layer is easily seen. The core martensite of Fe-24Mn steel carburized for 5 minutes is clearly shown in Figure 4.7.
Figure 4.5. Optical microstructures (20X magnification) of the carburized Fe-24Mn steel without HCl pre-treatment. The numbers in the brackets are the carburizing times in minutes. All polished samples were etched in a 3% nital solution for 15 seconds.
Figure 4.6. Optical microstructures (20X magnification) of the carburized Fe-30Mn steel without HCl pre-treatment. The numbers in the brackets are the carburizing times in minutes. All polished samples were etched in a 3% nital solution for 15 seconds.
Figure 4.7. Core martensite of Fe-24Mn steel sample carburized for 5 minutes: a) Surface and core and b) Core.
4.3.2 Concentration of Carbon and Manganese

When the carbon depth profile was measured using GDOES, three different zones were observed (Figure 4.8). Zone I shows a very high carbon with rapid drop with depth. Zone II indicates a low concentration with carbon rising with depth. Finally, Zone III exhibits a gradual decrease in carbon level with depth.

The carbon concentration of both steels has the highest value when carbon has diffused into a very thin depth (0 to 0.3 μm) below the surface as presented in Figure 4.8. This resulted from the high carbon potential due to high carbon activity in the gas phase [142].

![Figure 4.8. Zones in a carbon profile of the carburized Fe-Mn-C steels.](image)

The carbon and manganese concentrations in the carburized Fe-24Mn and Fe-30Mn steels as a function of depth below the surface are presented in Figures 4.9a and b. The results of carburizing Fe-24Mn and Fe-30Mn steels at
varying times show a region of a few microns of Zone I behavior. Only samples carburized for 30 and 60 minutes show Zone II behaviour though a plateau is evident. The sample carburized for 120 minutes shows a large Zone I with a low plateau (Figures 4.9a and b). For manganese in both steels, the concentration profiles show a rapid increase for a depth of 5 μm below the surface and followed by a gradual increase with depth varying between 5 and 60 μm (Figure 4.9).

Figure 4.9. Concentrations of carbon and manganese in carburized Fe-Mn-C steels: a) Fe-24Mn and b) Fe-30Mn. Numbers near to the curves are carburizing times in minutes.
A comparison of carbon concentration at a depth of 30 \( \mu \text{m} \) below the surface between these two steels is presented in Figure 4.10. At this point, both steels show a similar increase in carbon concentration with increasing carburizing times.

![Figure 4.10](image)

Figure 4.10. Concentration of carbon in carburized Fe-24Mn and Fe-30Mn steels at a depth of 30 \( \mu \text{m} \) below the surface.

### 4.3.3 Concentration of Oxygen

Figures 4.11a and b show the concentration of oxygen in Fe-24Mn and Fe-30Mn steel samples after carburizing for various times. All samples were initially ground with 600 \( \mu \text{m} \) grit grinding paper. The results from the GDOES analysis reveal that both steels have a low and consistent concentration of oxygen. High concentration of oxygen in both steels can be seen at approximately 10 \( \mu \text{m} \) below the steel surface. The presence of a small amount of oxygen in these steels is suggested to be due to handling and cooling the samples in air.
Figure 4.11. Concentration of oxygen in carburized Fe-Mn-C steels as a function of depth below the surface: a) Fe-24Mn and b) Fe-30Mn.
4.3.4 Non-uniform Carburizing Fe-24Mn and Fe-30Mn Steels

Repeat tests for the Fe-24Mn and Fe-30Mn steels carburized for 60 minutes showed regions where no carburization occurred. This is illustrated in Figure 4.12. In these cases, only one side of the samples is carburized. It is not understood what cause this but it may relate to oxide layer formation. A number of carburizing tests were performed in an attempt to avoid this. It was decided to continue carburizing using a HCl treatment to activate the surface.

Figure 4.12. Optical microstructures (5X magnification) showing the inconsistency of carbon concentration in Fe-24Mn and Fe-30Mn steels carburized for 60 minutes. The samples were etched in a 3% nital solution for 15 seconds.
4.4 Characterization after Carburizing with HCl Pre-treatment

4.4.1 Microstructure

Internal oxidation during carburizing contributes to the spotty carburization [182]. In addition to the hydrocarbon gases, a small amount of oxygen is inevitably present, causing surface oxidation during carburizing. Manganese form oxide on austenite grain boundaries to a depth of 10 to 20 μm when exposed to a gas carburizing atmosphere [139]. These are some possible reasons that can be related to the non-uniform carburizing of high manganese steels (Figure 4.12).

The carburizing without HCl pre-treatment was discontinued due to inconsistency in concentration of carbon in Fe-24Mn and Fe-30Mn steels. A new step was added that involved introducing a gas mixture of 10% volume concentration of HCl for 10 minutes before carburizing. The experimental details were described in Section 3.5.2 (Chapter 3). After activation in gaseous HCl, the steel samples were heated in a mixture of propane and nitrogen at a relatively high temperature of 930°C for 30 minutes.

After carburizing with HCl pre-treatment, three different layers were observed (Figure 4.13). The first layer, identified as Layer 1, is the ‘porous layer’; Layer 2 is the ‘carbide layer’ and Layer 3 is ‘carbon diffusion layer’ (Figure 4.13). The surface carbide layer observed in the samples were formed due to a higher carbon content at the surface (4 to 6 wt %) after carburizing for longer times (60 and 120 minutes). The porous layer is evidently a product of the reaction with HCl at the surface during the pre-treatment.
Figure 4.13. Various layers (100X magnification) below the surface of the a) Fe-24Mn and b) Fe-30Mn steels carburized for 120 minutes with HCl pre-treatment. The samples were etched in a 3% nital solution for 15 seconds.

The polished cross-sections of the carburized Fe-24Mn and Fe-30Mn steel samples obtained were examined by an optical microscope are displayed in Figures 4.14 and 4.15, respectively. The figures show an increase in the carbon diffusion layer (Layer 3) for both steels with increasing carburizing times. The difference in microstructure in the steels is subjected to the carburization. The low manganese steel has a core made of ε-martensite (Figure 4.14), whereas the high manganese content remains austenitic (Figure 4.15).
Figure 4.14. Optical microstructures (10X magnification) of the carburized Fe-24Mn steel with HCl pre-treatment. Numbers in the brackets are the carburizing times. All polished samples were etched in a 3% nital solution for 15 seconds.
Figure 4.15. Optical microstructures (10X magnification) of the carburized Fe-30Mn steel with HCl pre-treatment. Numbers in the brackets are the carburizing times. All polished samples were etched in a 3% nital solution for 15 seconds.
The proportion of diffusion carbon layer to the carburized sample thickness was determined from the optical microstructure images and these values are given in Figure 4.16. The carburized layers of the Fe-30Mn steel exhibit a slightly greater depth than that of those obtained in Fe-24Mn steel for most conditions. This is possibly related to the decreasing of carbon activity due to higher manganese content in the Fe-Mn-C steel. These depths will be employed to rationalize the strength of the present samples.

![Figure 4.16](image)

Figure 4.16. Proportion of carbon layer at the surface and the core of the carburized Fe-24Mn and Fe-30Mn steels.

The weight gain was determined as a function of carburizing time and this is plotted as a function of carbon layer depth in Figure 4.17. Both steels show an increase in weight gain with increasing thickness of carbon layer which corresponds to their carburizing times. Other than 5 minutes carburizing time, it can be seen that weight gain provides a reasonable means of monitoring carburization in these steels. The plot in Figure 4.17 can be used to evaluate carburization by the increase in weight of the samples.
Figure 4.17. Weight gain of the Fe-24Mn and Fe-30Mn steels carburized at varying times as a function of depth of carbon layer below the surface. Numbers near to the data points are the carburizing times in minutes.

The carbon concentration at the surface (a depth of 20 \( \mu \text{m} \)) after carburizing with HCl pre-treatment for various carburizing times is shown in Figure 4.18. The carbon concentration increases with increasing carburizing times and after 60 minutes the concentration exceeds 4%. This is consistent with the formation of carbides seen in Layers 1 and 2.
Figure 4.18. Carbon concentration at the surface (a depth of 20 μm) of the carburized Fe-24Mn and Fe-30Mn steels as a function of carburizing time.

4.4.2 Depth Profile

Concentrations of carbon in Fe-24Mn and Fe-30Mn steels carburized with a HCl pre-treatment are shown in Figures 4.19 and 4.20, respectively. The three zones identified in Figure 4.8 are evident in many cases. The carbon concentration profiles are very high at the surface (5 – 20%) and rapidly drop for the first 5 μm beneath the surface for all steel samples of both steels (Zone I). This is probably due to a high driving force for carbon transfer at the furnace-metal interface at the beginning of carburizing. The profiles were also observed to exhibit ‘up-hill diffusion’ (Zone II) followed by a more typical carbon diffusion region (Zone III). At the initial stage of Zone III, the carbon concentrations increase with increasing carburizing times. While the HCl treatment prevented the occurrence of uncarburized patches, some variability is still evident.
Figure 4.19. Concentration of carbon in carburized Fe-24Mn steel with HCl pre-treatment. Numbers near to the curves are the carburizing times in minutes.

Figure 4.20. Concentration of carbon in carburized Fe-30Mn steel with HCl pre-treatment. Numbers near to the curves are the carburizing times in minutes.
4.4.3 HCl Affected Zone – Porous Layer

The average depth of the ‘porous layer’ was measured from the optical microstructure images and the results are given in Figure 4.21. The depths of the porous layer in the Fe-24Mn steel were consistently lower than in the Fe-30Mn steel. A greater depth of the porous layer is observed for longer times, so it evidently grows slightly during carburizing despite being formed during the pre-treatment.

Figure 4.21. Depth of porous layer below the surface of the carburized Fe-24Mn and Fe-30Mn steels with HCl pre-treatment as a function of carburizing time.

4.4.4 Formation of Surface Carbide

The surface carbides are shown in the micrographs in Figures 4.22 and 4.23 for carburizing with a HCl pre-treatment. It can be seen that the thickness of carbide layer in both steels increases consistently with increasing
carburizing times from 15 to 120 minutes. Surface carbide formation is not observed below the porous zone in either sample carburized for 5 minutes. Nine measurements for carbide layer below the surface were carried out at 50 μm intervals. The results of XRD (Figures 4.27 and 4.28) evidence that iron and manganese carbide were observed in both Fe-24Mn and Fe-30Mn steels samples carburized for 120 minutes (Figures 4.22b and 4.23b).

![Optical microstructures](image)

a) Fe-24Mn (5 minutes).  

b) Fe-24Mn (120 minutes).

Figure 4.22. Optical microstructures (100X magnification) of carbide formation below the surface of the carburized Fe-24Mn steel. Numbers in the brackets are the carburizing times: a) 5 minutes and b) 120 minutes. All polished samples were etched in a 3% nital solution for 15 seconds.
Figure 4.23. Optical microstructures (100X magnification) of carbide formation below the surface of the carburized Fe-30Mn steel. Numbers in the brackets are the carburizing times: a) 5 minutes and b) 120 minutes. All polished samples were etched in a 3% nital solution for 15 minutes.

The mean depth of carbide formation is found to increase first rapidly then more slowly with increasing carburizing times (Figure 4.24).

Figure 4.24. Depth of carbide below the surface of the carburized Fe-24Mn and Fe-30Mn steels with HCl pre-treatment as a function of carburizing time.
The surface carbide formation at the surface of the tested steels was confirmed by XRD analysis. Cu-K\(_\alpha\) radiation was employed. The chemical composition present in the Fe-24Mn and Fe-30Mn steels before and after carburizing was identified using a database provided by X-Pert High Score Plus Software. The phases corresponding to the XRD peaks of the Fe-24Mn and Fe-30Mn steels before carburizing are presented in Figures 4.25 and 4.26, respectively. It can be seen that the samples are dominated by \(\varepsilon\)-Fe and \(\gamma\)-Fe, respectively. The Fe-24Mn steel shows a higher intensity in \(\varepsilon\)-martensite and Fe-30Mn steel clearly displays a higher amount of austenite. The peaks corresponding to the diffraction of austenite shift with increasing in manganese content from 24 to 30 wt %. As noted in the literature review, the \(\varepsilon\)-martensite start temperature drops at room temperature for manganese levels greater than 24 wt %.

Figure 4.25. XRD patterns of cold rolled and annealed (without carburizing) Fe-24Mn steel.
Figure 4.26. XRD patterns of cold rolled and annealed (without carburizing) Fe-30Mn steel.

The phases identified by XRD showed that the Fe-24Mn and Fe-30Mn steels carburized for 120 minutes were dominated by the presence of (Fe + Mn)$_3$C (Figures 4.27 and 4.28). The analysis was performed just below the steel surface and the theoretical value of the attenuator length was calculated to be 1.5 to 5.0 μm for 2-theta angle of 40 to 90°. This is quite consistent with optical microstructure images.
Figure 4.27. XRD patterns of carburized Fe-24Mn steel for 120 minutes.

Figure 4.28. XRD patterns of carburized Fe-30Mn steel for 120 minutes.
4.4.5 Manganese Profile

Concentration of manganese in Fe-24Mn and Fe-30Mn steels is depleted near the surface in a region 20 to 40 µm below the surface, respectively (Figure 4.29). The depth of manganese depletion is similar in magnitude to the depth of the porous layer and this will be discussed later. However, for the corresponding carbon profiles, the peak in concentration of carbon below the surface in both steels occurs just prior to the depth at which the manganese level attains its nominal value.

Figure 4.29. Concentration of carbon and manganese in Fe-24Mn and Fe-30Mn steels carburized for 60 minutes with HCl pre-treatment.
4.4.6 SEM-EDX Analysis

Investigation of the segregation of manganese was performed using SEM equipped with EDX detector. A manganese distribution in Fe-24Mn and Fe-30Mn steels using a spot scanning method is shown in Figure 4.30. The average composition of manganese is observed in both steels. This is resulted from a higher proportion of manganese added into the furnace during casting to avoid its losses when melted at high temperature. Overall, the results of SEM-EDX revealed a degree of segregation of manganese in homogenized and carburized Fe-24Mn and Fe-30Mn steels for 120 minutes. The longest carburizing time (120 minutes) was chosen to investigate the change in manganese level of both steels. The plots of manganese profiles show a minimal variation in manganese level. On the other hand, the loss in manganese content is low. The variation of ± 0.5 to 1.0 % in manganese seem to be responsible for the banding (dark/light shadowing) on the microstructure evident in Figure 4.4 above.

Figure 4.30. Concentration of manganese through a cross-section of the Fe-24Mn and Fe-30Mn steels measured by SEM-EDX spot scanning: 1) homogenized at 1180°C for 10 hours and 2) carburized for 120 minutes.
4.4.7 Grain Size

The aim of the next chapter is to relate the structure to the properties. For this, the grain size is required. How the grain size of the Fe-30Mn steel before carburizing relates to the thickness after cold rolling and annealing is shown in Figure 4.31. The grain size of this steel decreases from 90 to 35 μm after cold rolling from 4.0 to 1.5 mm in thickness. For subsequent processing, the thickness of the prepared Fe-30Mn steel plate was chosen to be 1.5 mm with the average grain size is approximately 35 μm.

Figure 4.31. Grain size of the Fe-30Mn steel as a function of sample thickness after cold rolling and annealing at 1000°C for 30 minutes.

Carburizing at high temperature typically results in grain growth [57]. In this work, there was minimal effect on the grain size of these steels when carburizing at 930°C with varying durations. The heating during carburizing increases the average grain size of the cold rolled and annealed Fe-30Mn steel from 35 to about 75 μm. Both Fe-24Mn and Fe-30Mn steels show a slight increase in grain size with increasing carburizing times from 5 to 15 minutes and from 30 to 120 minutes (Figure 4.32). The results show that at this
temperature, the grain size ranges between 60 and 75 μm. The grain size of the carburized Fe-24Mn and Fe-30Mn steels ranges from 70 to 90 μm after annealing at 1000°C for 30 minutes under argon atmosphere.

Figure 4.32. Various grain sizes of the Fe-24Mn and Fe-30Mn steels before and after carburizing.

4.5 Carburizing and Annealing

This section describes the Fe-24Mn and Fe-30Mn steel samples which were annealed at 1000°C for 30 minutes after carburizing at varying times. The carbon profiles of these samples are analyzed. The change in the microstructure of these steels is shown in Figure 4.33. The structure shows that the surface and the core of the Fe-24Mn steel contain austenite, and as shown in Figure 4.33, the grain size has coarsened by 5 – 15%.
a) Fe-24Mn.  

b) Fe-30Mn.

Figure 4.33. Microstructures (10X magnification) of the Fe-24Mn and Fe-30Mn steels which were carburized for 30 minutes and annealed at 1000°C for 30 minutes. Both samples were etched in a 3% nital solution.

4.5.1 Concentration of Carbon

The GDOES carbon profiles of carburized and annealed steel samples are shown in Figure 4.34. As intended, the carbon concentration gradient has been homogenized through the sample thickness in both steels.

The highest carbon concentration in the Fe-30Mn steel was demonstrated by the sample which was carburized for 60 minutes. For the Fe-24Mn steel, 120 minutes gave the highest concentration. This is evidently due to the inherent variation that is still part of the process.
Figure 4.34. Carbon concentration in carburized and annealed (1000°C, 30 minutes) steel samples: a) Fe-24Mn and b) Fe-30Mn. The numbers near to the curves are the carburizing times in minutes.
The average carbon contents of the carburized and annealed Fe-24Mn and Fe-30Mn steels as a function of carburizing time are plotted in Figure 4.35. Clearly, the treatment has been successful in generating a series of samples with different carbon levels.

![Figure 4.35. Carbon concentration in carburized and annealed Fe-24Mn and Fe-30Mn steels as a function of carburizing time.](image)

### 4.6 Discussion

The present chapter has shown that carburizing can be achieved in high manganese TWIP steels. Key to this success is a HCl pre-treatment step. Higher and consistent carbon concentrations are observed in the steels (as in Figure 4.18) when carburized after HCl pre-treatment. The structures produced have been characterized to a level required for correlation with the mechanical properties, which will be presented in the next chapter. However, a
number of phenomena have come to light that require further discussion. These are:

i) the apparent ‘up-hill’ diffusion of carbon in Zone II of the carbon profile.

ii) the impact of the HCl treatment on the structure and composition profile.

4.6.1 ‘Up-hill’ Diffusion of Carbon

The concentrations of carbon and manganese in Fe-24Mn steel carburized for 120 minutes as a function of depth below the surface are given in Figures 4.36a and b, respectively. The manganese concentration profile shows a rapid increase for a depth of 18 μm below the surface (0 to 17 wt % manganese) and followed by a gradual increase with depth varying between 18 and 120 μm (~24 wt % manganese).

The measurements of carbon profile taken by GDOES indicated an ‘up-hill’ diffusion. It is clear that the ‘up-hill’ carbon diffusion Zone II falls within the manganese depletion zone. This was evidenced by the early work by Darken [167] and later by Reger at el. [165] on the diffusion of carbon in austenite steels. It is thus suggested that in carburizing, the ‘up-hill’ diffusion of carbon is related to manganese depletion near the surface [183]. Manganese decreases the carbon activity, so lower manganese contents near the surface increase the activity coefficient of carbon. Thus, a ‘down-hill’ gradient in carbon activity can be maintained despite lower carbon levels in the manganese depleted region.

Manganese and carbon profiles can be correlated at a depth ranges between 10 and 18 μm below the surface. The ‘uphill’ diffusion of carbon in carburized Fe-24Mn steel is observed when manganese concentration is between 7 and 17 wt %.
Figure 4.36. Concentration of a) carbon and b) manganese below the surface of the Fe-24Mn steel carburized for 120 minutes. Numbers near to the curve are the zones of the carbon profile identified above.
4.6.2 Effect of HCl Pre-treatment

Another factor that influences the quality of carburizing is surface contamination. To avoid this, a HCl pre-treatment was used by Agarwal et al. [184] and Uberti et al. [185] followed by carburizing their steel (low carbon high alloy grade). The addition of HCl pre-treatment is an important step in achieving successful carburization in the present work. In this section, the HCl treatment is examined in more detail. Additional steel samples were carburized using the same method mentioned in Chapter 3 (Section 3.5.2) except the HCl pre-treatment was varied in time (2 and 5 minutes). The carbon and manganese concentrations in both steel samples were measured and their microstructures were analyzed and compared to samples which were carburized using a 10 minute HCl pre-treatment.

The porous layers formed in these tests are shown in Figure 4.37. It is seen that the porous layer increases in depth with time of HCl pre-treatment (see plot in Figure 4.38). This is consistent with the idea that the porosity relates to the reaction of the HCl with the steel surface prior to carburizing.
Figure 4.37. Porous layer (100X magnification) below the surface of the Fe-24Mn and Fe30Mn steel samples carburized for 30 minutes with HCl pre-treatment for various times: a), b) 2; c), d) 5 and e), f) 10 minutes. All polished samples were etched in a 3% nital solution for 15 seconds.
Figure 4.38. Porous layer below the surface of the Fe-24Mn and Fe-30Mn steels carburized for 30 minutes as a function of the HCl flow time.

The effects of HCl pre-treatment on the carbon profile are displayed in Figure 4.39. The results show that the varying times of HCl pre-treatment lead to variation in carbon concentration of both steels at a depth lower than 40 μm. At 80 μm below the surface the carbon levels are similar. No clear conclusion can be drawn other than that the 5 and 10 minutes treatments led to more similar profiles than the 2 minutes treatment. Figure 4.40 shows the impact of HCl treatment on manganese level. The loss in manganese concentration at the surface of the Fe-24Mn and Fe-30Mn steels over the depth below the surface is higher (approximately 20 μm) when carburized with HCl pre-treatment for a longer time (10 minutes) (Figure 4.40). This effect appears to be more systematic and suggests that the manganese depletion relates to the HCl treatment. In particular, it is likely that the porous zone reflects the erosion of manganese oxides and a more certain conclusion is outside of the present scope.
However, the point here is the porous layer can be reduced by HCl activation time, while maintaining the carburizing benefit. This has been proven by a consistent carbon concentration resulting from the carburizing of all steel samples with various HCl activation times (Figures 4.39 and 4.40). During carburizing, flow rate and time of HCl in the furnace must be taken into account to minimize the formation of porous layer that can result in the loss of manganese in the Fe-24Mn and Fe-30Mn steels.

Figure 4.39. Concentration of carbon below the surface of the steels carburized for 30 minutes. Numbers near to the curves are the HCl flow duration in minutes: a) Fe-24Mn and b) Fe-30Mn.
Figure 4.40. Concentration of manganese below the surface of the steels carburized for 30 minutes. Numbers near to the curves are the HCl flow duration in minutes: a) Fe-24Mn and b) Fe-30Mn.
4.7 Conclusions

The work done in this chapter can be concluded as follows:

- In this experiment, the use of HCl treatment prior to carburizing provided more consistent carbon concentrations in the two high carbon manganese steels studied. At the same time, the HCl treatment created a porous layer at the surface. The thickness of the porous layer increased with increasing HCl treatment time. The treatment also led to depletion of manganese near to the surface.

- The carbon concentration profile for most of the carburized samples can be categorized into three zones: Zone I – high carbon with rapid drop with depth; Zone II – low carbon concentration with carbon rising with depth and Zone III – normal decrease in carbon level with depth. The carbon diffusion in Zone II is ‘up-hill’ because carbon diffuses against the concentration gradient in these steels.

- The ‘up-hill’ diffusion of carbon can be understood in terms of the reduction in carbon activity coefficient caused by the presence of manganese. Near the surface, the manganese levels are low and so here the activity coefficient of carbon is high compared to the core. So, despite the high carbon activity near the surface, the observed carbon concentrations are low in Zone II.
Chapter 5: Mechanical Properties

5.1 Introduction

This chapter investigates the mechanical properties of the carburized Fe-24Mn and Fe-30Mn steels. The main concern is the relationship between the structure and the properties. The influence of carbon concentration and distribution on the mechanical properties is examined.

5.2 Mechanical Properties of the Carburized Steels

5.2.1 Micro-hardness

Micro-hardnesses of the hot rolled (4.0 mm) and cold rolled (2.6 mm, 2.0 mm and 1.5 mm) Fe-24Mn and Fe-30Mn steels are presented in Figure 5.1. The cold rolled samples without annealing show an increase in micro-hardness with decreasing sample thickness for both steels. This reflects work hardening.

The Fe-24Mn steel displays higher micro-hardness values overall.
Figure 5.1. Micro-hardness of hot rolled (4.0 mm) and cold rolled (2.6, 2.0 and 1.5 mm) Fe-24Mn and Fe-30Mn steels before carburizing. The data shown are averages of three measurements at the surface and core. Thicknesses of rolling in mm are given inside the histogram.

The variation of micro-hardness within the thickness of the samples is shown in Figures 5.2 and 5.3. The difference in behaviour of these steels described in the previous chapter is confirmed in these figures. The Fe-24Mn steel carburized for 5 to 60 minutes has a higher micro-hardness at the core than at the surface. For a carburizing time of 120 minutes, the Fe-24Mn steel shows a higher micro-hardness at the surfaces compared to at the core. The micro-hardness of the Fe-30Mn steel samples is higher at the surface than at the core for all carburizing times.
Figure 5.2. Micro-hardness at the surfaces (100 μm below the surface) and core of as-carburized samples: a) Fe-24Mn and b) Fe-30Mn. The thickness of both steel samples is 1.5 mm. Averages of three measurements.
Vickers hardness tests were performed on the carburized Fe-24Mn and Fe-30Mn steels samples at different depths below the surface. The distributions of micro-hardness over the sample thickness are presented in Figure 5.3. These profiles reveal hardening in the carbon rich layers for the Fe-30Mn steel and softening for the Fe-24Mn grade (for carburizing ≤ 60 minutes). 5 measurements were made at each depth, with some indentations possibly being in the grain and some others possibly being at grain boundaries of the samples. The mean of the measured hardness values of Fe-24Mn steel carburized for 5 and 30 minutes show a drop at distance of 100 and 400μm, respectively below the surface before increasing towards the core of the samples. This is due to carbon effect that stabilizes the austenite near the surface while maintaining a ‘hard’ martensite core. The plots of micro-hardness value of Fe-30Mn steel decrease with increasing the depth. This is evidently an effect that relates to solute strengthening due to carbon in austenite and to the higher hardness of ε-martensite compared to austenite.

Figure 5.3. Typical of micro-hardness profile below the surface of the Fe-24Mn and Fe-30Mn steels carburized for 5, 30 and 120 minutes.
5.2.2 Tensile Testing

In order to examine the effect of carbon level and distribution on the mechanical properties of the Fe-24Mn and Fe-30Mn steels, two groups of the samples for tensile testing were prepared from the cold rolled plate of 1.5 mm thick. First, samples were carburized without annealing, second, the samples were carburized and annealed. Tensile testing for the steel samples without carburizing was also carried out for comparison.

Tensile results presented in Figures 5.4 and 5.5 give an overview of the stress-strain behaviors of the carburized Fe-24Mn and Fe-30Mn steels. The cold rolled and uncarburized samples reveal the high strength of a worked ε-martensite structure in Fe-24Mn grade. However, as expected these cold worked samples display low ductility. Carburizing is seen to raise the strength by a maximum of ~200 MPa. However, ductility is seen to drop at higher carburizing times. For both steels, most favorable ductility is shown in the samples which were carburized for 30 minutes.

Mechanical twinning and dislocation glide are also expected to exist in the deformation of the carburized Fe-24Mn steel at room temperature with a strain rate of $10^{-3}$ s$^{-1}$. This is evident by the plot of stress-strain curves of Fe-24Mn steel, which show higher strength compared to Fe-30Mn steel. When manganese content is relatively high, the deformation of Fe-30Mn steel is found to be a dominant by only dislocation glide. This is in agreement with the statement by Bouaziz et al. [2] and the work done by Allain et al. [9].
Figure 5.4. True stress-true strain curves of as-carburized Fe-24Mn steel without annealing. Numbers near to the curves are carburizing times in minutes.

Figure 5.5. True stress-true strain curves of as-carburized Fe-30Mn steel without annealing. Numbers near to the curves are carburizing times in minutes.
5.2.3 Yield strength and Ultimate Tensile Strength

Yield strength as a function of carburizing time is shown in Figure 5.6. Initially, before carburizing, the Fe-24Mn steel has a higher yield strength compared to the Fe-30Mn steel. The yield strength of both steels increases with increasing carburizing times after 5 minutes of carburizing. For the Fe-24Mn steel, a sharp reduction in yield strength is observed after carburizing for 5 minutes. For the Fe-30Mn steel, a steady increase in yield strength with increasing carburizing times is seen. Both steels display similar values of yield strength after 15 minutes of carburizing.

Figure 5.7 plots the variation in ultimate tensile strength as a function of carburizing time. For each carburizing time, the Fe-24Mn steel displays a higher ultimate tensile strength compared to the Fe-30Mn steel. For the Fe-24Mn steel, the ultimate tensile strength value is largely insensitive to carburizing time. In contrast, the Fe-30Mn steel shows a steady increase in ultimate tensile strength with increasing carburizing times up to 30 minutes.

Figure 5.6. Yield strength of as-carburized Fe-24Mn and Fe-30Mn steels as a function of carburizing time.
Figure 5.7. Ultimate tensile strength of as-carburized Fe-24Mn and Fe-30Mn steels as a function of carburizing time.

The effects of carburizing time on the average uniform elongation and average total elongation are illustrated in Figure 5.8. From this figure, the Fe-24Mn steel shows a higher uniform elongation and total elongation compared to the Fe-30Mn steel for carburizing longer than 5 minutes. The low uniform elongation and total elongation of the Fe-30Mn steel when carburizing time is 15 minutes is probably due to the sample condition as all ductility measures were low. Unfortunately, it was not possible to repeat the tests at this condition. The maximum uniform elongation for the Fe-24Mn grade is when the carburizing time is 30 minutes. After this, carburizing degrades the ductility, for both steels.
Figure 5.8. Average a) uniform elongation and b) total elongation of the carburized Fe-24Mn and Fe-30Mn steels at varying times without annealing.
Figure 5.9 shows the reduction in area of the Fe-24Mn and Fe-30Mn steels as a function of carburizing time. The reduction in area was determined by measurements of the fractured cross section. The data are scattered but the Fe-30Mn steel clearly has greater ductility than the Fe-24Mn steel prior to carburizing. Initially, there is a decrease in reduction in area of the Fe-30Mn steel with carburizing. The Fe-24Mn grade shows little change in reduction in area with carburizing time up to 30 minutes. For carburizing for 15 minutes and greater, the two grades display similar values.

Figure 5.9. Average reduction in area of the carburized Fe-24Mn and Fe-30Mn steels without annealing.
The Hollomon analysis was applied to the true stress-true strain data of the Fe-24Mn and Fe-30Mn steels samples and the results are shown in Figures 5.10a and b, respectively. The results show that this analysis failed to show the linear relationship between \( \log_{10} \sigma - \varepsilon \) over the entire uniform strain range. The slope of each curve \( \log_{10} \sigma - \varepsilon \) of both steels increases with increasing strain.

Figure 5.10. Hollomon analysis \( \log_{10} \) true stress – true strain) for carburized high manganese steels samples: a) Fe-24Mn and b) Fe-30Mn.
Next, the change of the instantaneous work-hardening exponent, n with true strain is presented Figures 5.11 and 5.12. The exponent ‘n’ in the constitutive equation is originally proposed by Ludwik [186] and modified by Hollomon [187] to describe stress-strain curves. The Hollomon analysis was applied to the true stress-true strain data of the present samples to establish the power law work-hardening exponent, n over strain intervals of 0.05. In this plot, a 1:1 trend is included. When the measured data intersect this line, the Considère criterion is satisfied and diffuse necking is expected. Clearly in all of the present samples, the Considère condition has been attained. It is seen that both steel samples which were carburized for 30 minutes attain to the highest n-values.

Figure 5.11. Work-hardening exponent, n for the carburized Fe-24Mn steel samples as a function of true strain.
The work-hardening rate, \( \frac{d\sigma}{d\varepsilon} \) of Fe-24Mn and Fe-30Mn steels samples carburized at varying times as a function of true stress for tensile deformation are plotted in Figures 5.13 and 5.14, respectively. The carburized Fe-24Mn steel samples show a decrease in work-hardening rate with true stress in the range of 500 to 800 MPa. Both Fe-24Mn and Fe-30Mn steels samples show a greater stress of approximately 1500 (1200 MPa) and 1350 MPa, respectively, when carburized for 30 minutes. When work-hardening rate is numerically equal to the stress, uniform elongation of both steels stop and necking is initiated as shown by the linear black line (Figures 5.13 and 5.14).
Figure 5.13. Work-hardening rate, $d\sigma/d\varepsilon$ for the carburized Fe-24Mn steel samples as a function of true stress.

Figure 5.14. Work-hardening rate, $d\sigma/d\varepsilon$ for the carburized Fe-30Mn steel samples as a function of true stress.
5.3 Discussion

This section discusses the influence of carbon gradient and level on the mechanical properties. Finally, the role of surface carbide is discussed.

5.3.1 Prediction of the Mechanical Properties of the Carburized Fe-24Mn Steel using a Law of Mixtures

A law of mixtures was first proposed by Voight to predict the mechanical properties such as Young's modulus, yield strengths and flow stresses of composite materials [188, 189]. This law has been used in many studies [188, 190-193] to correlate the properties of a sample with those of its constituents.

In what follows, the mechanical properties of the carburized Fe-24Mn and Fe-30Mn steels are analyzed using a law of mixtures approach. An idealized structure of the Fe-24Mn steel containing austenite and $\varepsilon$-martensite is illustrated in Figure 5.15. One of the key controlling parameters for yield stress at the surface and core of these steels is the proportion of the surface layer of the carburized steels. Previous work done by Pouranvani [192] proved that the yield and tensile strengths of the steel can be correlated with volume fraction of $\varepsilon$-martensite using this rule of mixtures.
Figure 5.15. Cross section of the carburized Fe-24Mn steel sample - constituent at the surface (austenite, γ) and at the core (martensite, ε). Area I (hatched) is the austenite high carbon layer below the surface. Area II is a region containing ε-martensite. C_s is the mean carbon level in Area I and σ is an applied stress in tensile testing. t_s is the thickness of the carburized layer, and t is the thickness of the sample.

The iso-strain law of mixtures is applied. Thus the following is given for yield stress:

$$\sigma_y = P \sigma_s + (1 - P)\sigma_c$$  \hspace{1cm} \text{Equation 5-1}$$

where P is the proportion of the surface layer, 2t_s/t (data in Figure 4.16). \(\sigma_s\) is the yield stress of the carburized surface layer and \(\sigma_c\) is the yield stress of the core.

As described above, the carburized Fe-24Mn and Fe-30Mn steel samples were annealed (1000°C, 30 minutes) in order to generate uniform
carbon levels throughout the sample thickness. These samples provide a reference for understanding the effect of carbon on mechanical properties.

The effects of annealing treatment on yield strength of carburized Fe-24Mn and Fe-30Mn steels are displayed in Figures 5.16 and 5.17, respectively. For a short carburizing time of 5 minutes, the yield strength of carburized and annealed Fe-24Mn steel is higher than that of the sample carburized and not annealed (Figure 5.16). However, at higher carburizing times (> 10 minutes), the samples which were carburized and not annealed show higher yield strengths. This difference arises because the core of the carburized samples remains in the harder $\varepsilon$-martensite phase after carburizing and before annealing. Once annealing has been performed, carbon level becomes uniform over the thickness and the entire thickness is occupied by the softer austenite phase. At lower carburizing time (5 minutes), it is probable that the soft austenite surface layer reverts to $\varepsilon$-martensite during the annealing treatment. Thus, after annealing the strength is increased.

Both sets of carburized Fe-30Mn steel samples show a consistent increase in their yield strength with increasing carburizing times (Figure 5.17). The annealing treatment is found to have an insignificant effect. This indicates that in this material the location of carbon over the sample thickness has little effect on strength.
Figure 5.16. Effect of annealing treatment on yield strength of the carburized Fe-24Mn steel.

Figure 5.17. Effect of annealing treatment on yield strength of the carburized Fe-30Mn steel.
This finding indicates that the law of mixtures equation given above is a realistic approximation, if the carbon effect on yield strength is approximately linear. Proof of this is as follows:

The law of mixtures equation presented above is:

$$\sigma = P_s \sigma_s + (1 - P_s P) \sigma_c$$  \hspace{1cm} \text{Equation 5-2}$$

Assume that the carbon effect is linear,

$$\sigma = KC + \sigma_0$$  \hspace{1cm} \text{Equation 5-3}$$

So that the law of mixtures becomes:

$$\sigma = P_s (KC_s + \sigma_0) + (1 - P_s) + (KC_c + \sigma_0)$$
$$= K(P_s C_s + (1 - P_s)C_c) + \sigma_0$$  \hspace{1cm} \text{Equation 5-4}$$

Now the total carbon content can be written as:

$$C_T = P_s C_s + (1 - P_s) C_c$$  \hspace{1cm} \text{Equation 5-5}$$

Substituting gives:

$$\sigma = KC_T + \sigma_0$$  \hspace{1cm} \text{Equation 5-6}$$

So it is seen that for a law of mixtures based on a linear yield stress–carbon relationship, the total carbon content is the controlling factor on yield stress.
For completeness, the ductility of the Fe-24Mn and Fe-30Mn steels is given by the plots of reduction in area as a function of carburizing time (Figures 5.18 and 5.19). It can be seen that in general the annealing treatment for 30 minutes increases the reduction in area. For the Fe-24Mn steel, this can be explained by the reduction in fraction of hard $\varepsilon$-martensite phase. For the carburized Fe-30Mn steel samples, the effect may relate to dissolution of a brittle surface carbide.

Figure 5.18. Effect of annealing treatment on the reduction in area of the carburized Fe-24Mn steel as a function of carburizing time.
Figure 5.19. Effect of annealing treatment on the reduction in area of the carburized Fe-30Mn steel as a function of carburizing time.

In analyzing the properties using the law of mixtures, a mean carbon level is needed to be assigned to the surface layer. To achieve this, the carbon profile for the Fe-24Mn steel was fitted in MATLAB. An example for the steel sample carburized for 30 minutes is shown in Figure 5.20. An average carbon content was determined from the fit. The average carbon levels of the carburized surface layer determined using this method are given in Table 5.1. The average carbon level at the core is assumed to be the same as in the initial sample before carburizing. Also shown in the table are the core fractions.
Figure 5.20. Comparison of carbon concentration between the calculation and experimental data of the Fe-24Mn steel carburized for 30 minutes.

The yield strength of $\varepsilon$-martensite is assumed to remain constant at 390 MPa, which is the yield strength of Fe-24Mn sample prior to carburizing. The yield strength of austenite is plotted against carbon in Figure 5.21 (using data from Figures 4.35 and 5.6). The relationship can be described by $\sigma = 130C + 260$. 
Figure 5.21. Influence of carbon on the yield strength of austenite, obtained from carburized and annealed samples. Numbers near to the data point are the carburizing times in minutes.

Table 5.1. Average carbon levels at the surface and the core of the carburized Fe-24Mn and Fe-30Mn steels.

<table>
<thead>
<tr>
<th>Steel</th>
<th>Carb. time (min)</th>
<th>Ave. C_s (wt %)</th>
<th>Ave. C_c (wt %)</th>
<th>Calculated $\sigma_s$ (MPa)</th>
<th>Calculated $\sigma_c$ (MPa)</th>
<th>Carbon layer (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-24Mn</td>
<td>5</td>
<td>0.47 ($\gamma$)</td>
<td>0.15 ($\varepsilon$)</td>
<td>321</td>
<td>390</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.62 ($\gamma$)</td>
<td>0.16 ($\varepsilon$)</td>
<td>341</td>
<td>390</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.87 ($\gamma$)</td>
<td>0.15 ($\varepsilon$)</td>
<td>373</td>
<td>390</td>
<td>56</td>
</tr>
<tr>
<td>Fe-30Mn</td>
<td>5</td>
<td>0.43 ($\gamma$)</td>
<td>0.16 ($\gamma$)</td>
<td>316</td>
<td>224</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.64 ($\gamma$)</td>
<td>0.17 ($\gamma$)</td>
<td>343</td>
<td>224</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>0.80 ($\gamma$)</td>
<td>0.16 ($\gamma$)</td>
<td>364</td>
<td>224</td>
<td>78</td>
</tr>
</tbody>
</table>
The predictions made using the data in Table 5.1 are shown in Figure 5.22. This agreement is reasonable, which shows this simple approach to be useful in predicting the yield strength of carburized samples.

Figure 5.22. Comparison of yield strength of a) Fe-24Mn and b) Fe-30Mn steels between the calculations using a law of mixtures and experimental results.
5.3.2 Ductility

The microstructure of the Fe-24Mn and Fe-30Mn steels carburized for 60 and 120 minutes (e.g. Figure 5.23) reveals that these steels have a high volume fraction of carbide right at the surface due to high carbon content (4 to 6 wt %). It is possible that this carbide impacts on the ductility. The annealing treatments resulted in a moderate increase in ductility (Figures 5.18 and 5.19) and it is possible that this relates to carbide dissolution. However, a series of tests performed on samples with polished surfaces (from which the carbide layer was removed) failed to reveal a systematic effect. Future work is

**TS 30 120**

Figure 5.23. Optical microstructure of carbide formation below the surface of the carburized Fe-Mn-C steel. This sample was etched in a 3% nital solution for 15 seconds.
5.4 Conclusion

The main findings in this chapter are listed below:

- All Fe-30Mn steel samples have higher micro-hardness at the surface than at the core for all carburizing times. For the Fe-24Mn steel, the micro-hardness at the core is greater when carburizing times are between 5 and 60 minutes. For longer times (> 60 minutes), this steel has the highest micro-hardness at the surface.

- The carburizing for a shorter time of 5 minutes significantly decreases the yield strength and the ultimate tensile strength of the Fe-24Mn steel. This is due to the formation of the softer austenite phase at the surface. For the Fe-30Mn steel, both yield and ultimate tensile strength increase with carburizing times.

- The ductility of the carburized Fe-24Mn steel increases with carburizing times up to 30 minutes. After this, the ductility drops.

- The ductility of the Fe-30Mn grade showed a variable ductility for low carburizing times but a clear drop was detected for carburizing times longer than 30 minutes.

- For the Fe-24Mn steel, carburized samples show higher strength than those with a uniform carbon distribution. But this comes with a drop in ductility.

- The influence of carburizing on the yield strength can be understood in terms of a simple law of mixtures model.
• For the Fe-30Mn steel, the yield strength is insensitive to the distribution of carbon. So carburizing can be used to create similar strengths as for conventional product.

• The most favourable combination of tensile strength and uniform elongation are seen in Fe-24Mn and Fe-30Mn steel samples carburized for 30 minutes.
Chapter 6: Exploring the Possibilities of Carburizing High Manganese Steels

This chapter focuses on exploiting carburizing for enhanced mechanical properties. Two experiments were carried out:

a) Two-stage carburizing of the Fe-24Mn and Fe-30Mn steels.

b) Cold rolling of carburized Fe-24Mn steel.

6.1 Two-stage Carburizing Fe-24Mn and Fe-30Mn Steels

6.1.1 Introduction

It is possible that surface carbide formation deteriorates the ductility (Chapter 5). In an attempt to avoid this, carburizing was conducted at two different carbon potentials.

6.1.2 Experimental Procedures

Both Fe-24Mn and Fe-30Mn steels were carburized for 30 minutes. Initially, the mixture of propane (0.26 m\(^3\)/h) and nitrogen (1.22 m\(^3\)/h) gases was ‘high’. After 15 minutes, the flow rate of these gases was decreased to 0.13 m\(^3\)/h for propane and increased to 1.60 m\(^3\)/h for nitrogen. After carburizing with HCl, the samples were rapidly quenched in water. Characterization was performed using optical microscopy and Glow Discharge Optical Emission Spectrometry (GDOES).
6.1.3 Results

6.1.3.1 Microstructure

Figure 6.1 shows the microstructures of the samples. In two-stage carburizing, a decrease of flow rate of propane results in a lower carbon activity between the surface and core of steel. No carbide layer can be seen on either of the steels. However, the porous layer from the HCl treatment is still present. Lower carbon diffusion is expected to suppress the formation of carbide below the surface of these steels. This is consistent with the results of GDOES analysis (Figure 6.3).

The critical carbon concentration for carbide forming is found when the Fe-24Mn and Fe-30Mn steels samples were carburized for longer times (Section 5.3.2). Higher carbon content results in the brittleness of these steels. This finding is consistent with the result of lower ductility when the steels were carburized for longer times.

Figure 6.1. Optical microstructures (100X) showing a porous layer but an absence of carbide below the surface of the Fe-24Mn and Fe-30Mn steels carburized for 30 minutes using two-stage carburizing. The samples were etched in a 3% nital solution.
6.1.3.2 Concentration of Carbon, Manganese and Iron

Figure 6.2 shows the concentration of carbon which resulted from the two-stage carburizing is lower than that in the samples which were carburized previously (Section 3.5.2) with constant flow rate of propane gas for 30 minutes, 0.26 m³/h (Figure 6.3). Lower volume of propane (0.13 m³/h) for the last 15 minutes during carburizing causes significant decreases in carbon potential of the furnace. The carbon concentration at the surface of the Fe-24Mn and Fe-30Mn steels ranges between 0.6 and 0.8 wt %. At 30 µm below the surface, the Fe-24Mn and Fe-30Mn steels undergoing one-stage carburizing show a higher carbon concentration than their counterparts undergoing two-stage carburizing. The carbon concentrations for one-stage carburizing of these steels are 1.95 and 1.5 wt %, whereas two-stage carburizing results in 0.65 and 0.75 wt %, respectively.

The concentrations of iron and manganese are given in Figure 6.4. Both steels show a lower concentration of manganese beneath the surface and as mentioned above, this due to the loss of manganese during the HCl treatment.

![Figure 6.2. Concentration of carbon in Fe-24Mn and Fe-30Mn steel samples as a function of depth below the surface after two-stage carburizing for 30 minutes.](image-url)
Figure 6.3. Comparison of carbon concentration between the Fe-24Mn and Fe-30Mn steels carburized for 30 minutes using one-stage (solid line) and two-stage (dashed) carburizing procedure.

Figure 6.4. Concentration of iron and manganese in Fe-24Mn and Fe-30Mn steels as a function of depth below the surface after two-stage carburizing for 30 minutes. Numbers near to the curves show the manganese contents (wt %) in the steels.
6.1.4 Discussion

The carbon potential of carburizing atmosphere has an influence on carbon profiles [194]. The aim of this experiment is to examine the surface carbide formation after carburizing at a different carbon potential (two-stage carburizing). The same carburized procedure was used except a different flow rate of propane and nitrogen gases was applied. The purpose of high carbon potential in the first phase of carburizing is to provide higher driving force for carbon transfer from the furnace to the steel surface. However, in the second stage a lower carbon potential was introduced in this work is to prevent high carbon levels building up at the surface. The three zones identified in Figure 4.7 are also evident in this case. The results from the optical microstructure and the GDOES analysis show that this technique can be used to avoid carbide precipitation in the steel. This is also explained by Dragomir and Druga [162]. In this work, a case depth of ~350 μm was obtained in 30 minutes of carburizing. As mentioned above, both steel samples show a carburized layer without the presence of carbide at the surface (as seen in Figure 6.1).

6.1.5 Conclusion

In this experiment, a lower carbon potential introduced in two-stage carburizing evident that the formation of surface carbide in both steels can be prevented.
6.2 Cold Rolling of Carburized Fe-24Mn Steel

One factor limiting the immediate implementation of TWIP steels is their relatively low yield strength especially when compared to existing advanced high strength steels. This is particularly important in the automotive sector for anti-crash assemblies where high yield strength values are essential. In this experiment, strength increases due to cold rolling are investigated. The layered structures may provide a useful strength-ductility balance.

6.2.1 Experimental Procedures

Carburized Fe-24Mn steel plates (60 mm x 10 mm x 1.5 mm) were prepared for cold rolling. The reduction per pass of all samples was set to 0.1 mm and the total reduction in thickness was 15% (0.2 mm). The plates were then cut into tensile gauge dimension, 25 mm x 5 mm and tested at room temperature with a strain rate of 0.001s⁻¹. Finally, microstructures of these samples were characterized.

6.2.2 Results

6.2.2.1 Microstructure

The austenite and ε-martensite layers in Fe-24Mn steel samples which were carburized for 5, 15, 30 and 60 minutes and cold rolled by 15% of total reduction are given in Figure 6.5.
Figure 6.5. Optical microstructures (10X magnification) of the carburized and cold rolled Fe-24Mn steel. Numbers in the brackets are the carburizing times in minutes. All polished samples were etched in a 3% nital solution for 15 seconds.

6.2.2.2 Micro-hardness

Figure 6.6 shows the micro-hardness at the surface and the core of the cold rolled carburized Fe-24Mn steel. There is a significant increase in micro-hardness when the carburized Fe-24Mn steel samples were cold rolled. The micro-hardness at the surface ranges between 390 and 450 HV for carburizing times of 5, 15, 30 and 60 minutes. The Fe-24Mn steel carburized for 60 minutes exhibits a lower micro-hardness at the surface than that of the
other samples due to higher amounts of retained austenite. The micro-hardness at the core of these samples containing \( \varepsilon \)-martensite phase increases with increasing carburizing times in the range of 400 to 550 HV.

![Micro-hardness graph](image)

Figure 6.6. Micro-hardness of the carburized and cold rolled Fe-24Mn steel.

6.2.2.3 Mechanical Properties

True stress-true strain curves of the carburized and cold rolled Fe-24Mn steel are presented in Figure 6.7. It can be seen that the true-strain for all samples is consistently increased relative to their true-stress when carburized for longer times and then cold rolled. A significant increase in true stress and true strain can be related to the strengthening during cold rolling.
Figure 6.7. True stress-true strain curves of the carburized and cold rolled Fe-24Mn steel samples. The numbers near to the curves are carburizing times in minutes.

Yield strength and ultimate tensile strength of these samples as a function of carburizing time is represented in Figure 6.8. The highest yield strength is shown in the sample which was carburized for 30 minutes. But this is due to an apparent difference in yielding behaviour. For strain > ~2%, the 60 minutes carburized sample displayed the highest strength.
Figure 6.8. Yield strength and ultimate tensile strength of the Fe-24Mn steel samples after carburizing at varying times and cold rolling.

The uniform total elongation and the reduction in area of the Fe-24Mn steel samples carburized at varying times and cold rolled are displayed in Figures 6.9 and 6.10. 30 minutes carburizing gives the highest elongation values. These will be compared to previous experiment in the next section.
Figure 6.9. Uniform elongation and total elongation of the Fe-24Mn steel samples after carburizing at varying times and cold rolling.

Figure 6.10. Reduction in area for the Fe-24Mn steel samples after carburizing at varying times and cold rolling.
6.2.3 Discussion

The comparison of yield strength and uniform elongation of the steels is plotted in Figure 6.11. For the Fe-24Mn steel, the samples show an increase in ductility but decrease in strength for lower carburizing times. For the Fe-30Mn steel, the strength-ductility increases for the sample carburized for the shortest time. This can be explained by the effect of carbon gradient that stabilizes the austenite in the samples which were carburized for shorter times. The present data is in agreement with the literature in which the presence of carbon in both steels changes the combination of the strength-ductility.

Both carburizing and cold rolling have a big role in controlling the properties of this steel. The strengths of the Fe-24Mn steel samples are consistently higher than that of the other samples with lower ductility. It is evident that the cold rolling is an interesting way to strengthen TWIP. This finding is in agreement with the work reviewed by Bouaziz et al. [2].
Figure 6.11. Comparison of yield strength and uniform elongation of the carburized and cold rolled high manganese steels. Numbers near to the data points are the carburizing times in minutes.

For better comparison, the plot of ultimate tensile strength (UTS) - uniform elongation (UE) of the steels is given in Figure 6.12. As seen, the large UTS-UE value is obtained for the steel sample carburized for 30 minutes. A trend of strengthening via carburizing accompanied by a loss of ductility is shown in the samples carburized for longer times. The various UTS-UE of the present work (Figure 6.12) can be explained by the effect of carbon gradient which decreases the uniform elongation of both Fe-24Mn and Fe-30Mn steels samples. For Fe-24Mn steel samples, carburizing for various times seem to have small changes in ultimate tensile strength between 850 and 900 MPa.
Figure 6.12. Comparison of ultimate tensile strength and uniform elongation of the carburized high manganese steels. Numbers near to the data points are the carburizing times in minutes.

6.2.4 Conclusion

In summary, the present work clearly shows that carburizing and cold rolling have a strong effect on strength-ductility of high manganese steels. Both of these factors combine to strongly reduce the Fe-24Mn steel sheet formability.
Chapter 7: Conclusions

The effect of carburizing on the microstructure and mechanical properties of high manganese steels has been studied. The conclusions that can be drawn from the work are listed below:

- Carburizing Fe-24Mn and Fe-30Mn steels was successful with the use of a HCl pre-treatment.

- The HCl treatment prevents patchy carburization but leads to a thin porous surface layer.

- In the Fe-24Mn steel, carbon diffusion caused the formation of a layered structure of ε-martensite and austenite, with austenite at the surfaces. In the Fe-30Mn steel, austenite is retained at all carburizing times, as would be expected.

- For both steels, carburizing for times up to 30 minutes had a positive effect on the combination of mechanical properties (higher yield strength, ultimate tensile strength and elongation). For carburizing times longer than 30 minutes, ductility was compromised.

- For the Fe-24Mn steel, a carbon rich surface gave a higher yield stress compared with the samples in which the same level of carbon was distributed over the thickness. The distribution of carbon over the sample thickness did not impact on the yield strength of Fe-30Mn alloy.
Most samples displayed a region of ‘up-hill’ carbon diffusion below the surface. This is explained by manganese depletion which raises the carbon activity coefficient near the surface.

Two-stage carburization was found to reduce the high carbon concentrations at the surface.

Cold rolled carburized Fe-24Mn samples, which posses a $\varepsilon$-martensite core and austenite surface show favourable ductility improvements whilst maintaining high as-rolled strengths.

### 7.1 Contributions to Original Knowledge

Much work has been studied on the effect of carbon level on microstructures and mechanical properties of high manganese steels. However, the effect of carbon gradient at the surface of these steels introduced through carburizing was unknown. There have not been any studies regarding the carburizing of these steels. This research has developed new understanding of the effect of carbon on the structure-property relationship of carburized TWIP steels.

The work showed, for the first time, how HCl treatment prior to carburizing avoids patchy carburization. This treatment removed an oxide layer but at the same time it created a porous layer at the surface. The thickness of the porous layer increased with increasing HCl treatment time and facilitated a manganese depleted layer.

The best carburizing method was found. This involved HCl pre-treatment for 5 minutes followed by carburizing for 30 minutes at 930°C under a nitrogen atmosphere in a fluidized bed furnace. The samples were quenched in water after carburizing.
Carbon diffusion against its concentration gradient was seen in the Fe-Mn-C steels. In this case, the ‘up-hill’ diffusion was determined to occur due to manganese depletion just beneath the surface. The effect arises from the increase in carbon activity coefficient in the low manganese region.

While the strength of the Fe-30Mn steel increased monotonically with carburizing, the influence of carbon on the austenite to martensite ($\gamma \rightarrow \varepsilon$) phase transformation meant that carburizing Fe-24Mn leads to a strength drop and then an increase with carburizing time.

For the Fe-30Mn steel, it was shown that the carburized samples without annealing have similar strength to those carburized samples that were annealed. This finding reveals that carbon gradient at the surface has little impact on strength. However, it tends to lower ductility.

For the Fe-24Mn steel, the presence of a $\varepsilon$-martensite core means that carburized samples show higher strengths.

The yield strengths of the carburized steels can be described approximately by a law of mixtures expression, which assumes a negligible influence of carbon on the strength of the $\varepsilon$-martensite over its range of stability in the present work.

This work also investigated the carburizing which performed at two levels carbon potentials. A ‘high’ and a ‘low’ carbon potential were introduced in two-stage carburizing evident that the formation of surface carbide in both steels can be prevented. A lower carbon potential in this experiment enabled a carbon rich layer to be formed free of significant carbide.

An important opportunity identified in this study is cold rolling of carburized Fe-24Mn steel. The steel has a hard core but soft surface and this gives reasonable ductilities following cold rolling.
7.2 Suggestions for Future Work

The strength and ductility of the carburized Fe-24Mn and Fe-30Mn steels in this study were promising.

It would be beneficial to suggest for the future work to study on:

- the effect of carburizing temperature on the microstructure and mechanical properties.

- the consistency of carbon potential in the furnace, which would affect the concentration of carbon.

- the formation of surface carbide when carburized for longer times. Further investigation on the carbon distribution through the austenite grain boundary and their effect on the structure-property relationship.

- the effect of volume fraction of austenite and $\varepsilon$-martensite on the mechanical properties of the carburized steel. This fraction will be useful to estimate the mechanical properties of this steel.
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