SECONDARY CARBIDE DISSOLUTION AND COARSENING IN 13% Cr MARTENSITIC STAINLESS STEEL DURING AUSTENITIZING

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ABSTRACT

Cutting blades and knives in various forms are manufactured from martensitic stainless steel strips. The manufacturing process of these cutting knives comprises a hardening heat treatment, cutting edge formation, and shaping into product dimensions. In a production environment, the hardening heat treatment is typically carried out continuously using an in-line heat treatment system. Such a heat-treatment process enables high production speed and efficient throughput. However, a high speed in-line heat-treatment process is very sensitive to raw material variations. Such variations may arise from differences among the manufacturing processes employed at raw material suppliers as well as shipment to shipment quality variations from a supplier. Some of these variations can be very subtle and might not have been fully understood by conventional material characterization techniques. The subtle material variations could cause differences in the response of the materials to the heat treatment, thereby potentially impacting the downstream manufacturability as well as the performance of the finished products. In addition, with the increasing demand for higher through-put production, optimizing the process parameters has become even more crucial. Therefore, the purposes of this work were to study the physical metallurgy of the hardening process and ultimately develop a simulation model to predict the kinetics of secondary carbide dissolution and coarsening during the austenitizing treatment of martensitic steel.

The steel studied in this work mainly contains 0.7 wt. % C and 13% of Cr, which is a non-AISI standard martensitic stainless steel. Detailed material characterization was carried out using
advanced quantitative metallographic techniques to characterize the subtle materials variations. The secondary carbide size distributions before and after the hardening process were characterized by scanning electron microscopy (SEM) and analyzed by computer assisted image analysis techniques. It was found that both the volume fraction and number of the secondary carbides decreased during the hardening treatment process, while the mean diameter remained nearly unchanged, indicating critical effects of Ostwald ripening on the final carbide size distribution. Historically, however, studies on the heat treatment of this martensitic stainless steel focused mainly on secondary carbide dissolution, while little attention is paid to carbide coarsening.

To better understand and ultimately provide a tool for the simulation of the concurrent occurrence of carbide dissolution and coarsening, mathematical carbide dissolution and coarsening model was developed incorporating a metallurgical kinetic theories of dissolution and Ostwald ripening. This was justified since most previous models were developed to predict only the mean carbide diameter and as such does not address the change in secondary carbide size distributions caused by concurrent dissolution and coarsening.

Comparison of simulated distributions with those determined experimentally indicates that both dissolution and coarsening indeed occur concurrently during the hardening process. It was found that during austenitization the average radius of carbide particles increases quickly as small carbide particles dissolve in the austenite, but increases only slowly once small particles have disappeared. The nearly constant carbide radius maintained after the disappearance of small particles reflects comparable rates of carbide dissolution and coarsening. The cumulative amount of carbide dissolution increases while the average radius remains nearly constant.
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1. Introduction

Martensitic stainless steels have been widely used for making swords, knives, scissors, cutting tools, surgical blades, and shaving blades due to its high corrosion resistance and superior hardenability. The process of making these cutting instruments using martensitic stainless steels has been evolved from hand-making with more than 60 process steps to fully integrated, computerized mass production that enables to produce the highest quality cutting instruments with efficient productivity.

Despite the highly established practice in the commercial mass production processes of martensitic stainless steel cutting products, the fundamentals of the materials, the processes and the phase transformation for making the cutting instruments had been studied to certain extents, yet have not been fully understood. An important aspect of such under-investigated material response is the dissolution and coarsening of secondary carbides during the austenitizing heat treatment in the in-line manufacturing process. The present research focused on the kinetics of carbide dissolution and coarsening which affects not only the properties of the final product, but also the manufacturing steps that follow the austenitizing heat treatment.
1.1 The history of stainless steel cutting instruments

The development of cutting instruments has paralleled mankind’s progress throughout history. They require a material with high hardness and good corrosion resistance. Imagine how labor intensive, difficult and costly it would be to our daily tasks if today’s cutting tools were not available.

The cutting instrument evolution in history is tightly connected with the hard materials availability for making them. Scientific researches and archaeological diggings had discovered that the first knives ever made by man were the sharp splinters that became in human use about 300,000 years ago. During the Stone Age, Flintstone was common and readily available. The sharp edges on these splinters formed a type of cutting implement that made skinning and hacking up animals killed in the hunt a lot easier. People of the late Stone Age used flint more than any other stones for making weapons and tools. In the Bronze Age, metals replaced stone slowly. Knives were made of copper and bronze when those metals came into use. The Iron Age began about 1000 BC. After 1432 BC, actual written records show that iron was used for weapons, knives and farm tools. Iron is one of the most common metals in the earth’s crust. It can be found almost everywhere, combined with many other elements, in the form of iron ore. Iron knife blades were far superior to any of their predecessors. Cutting and shaving knives, scythes and sickles, then ultimately scissors with springs completed the list of cutting implements being made by the end of the Iron Age. In the late 18th century, the nature of the iron, cast iron and steel relationship and the role of carbon in the preparation and characteristics of these three materials were precisely determined. Today, iron is referred to as “low-carbon steel, with carbon content less than 0.01%.
The plain carbon and alloy steels had displaced other materials for the blades of instruments for cutting. The best knives were forged from high-carbon steel before stainless steel was discovered.

Stainless steel was first discovered in 1912 by accident because their unusual resistance to corrosion\(^2\). Henry Brearley, an English metallurgist, was the first used “stainless steel”. The first true stainless steel was melted on August 13, 1913. It contained 0.24% carbon and 12.8% chromium. To examine the grain microstructure of the steel, Brearley used nitric acid as the etching reagent and found that this new steel strongly resisted chemical attack. He then exposed samples to vinegar and other food acids such as lemon juice and found the same result. Brearley immediately realized the practical use of the new material that he had discovered. It did not take long for stainless steel to be used to make cutlery. In 1919 – 1923, Sheffield cutlers started regular production of stainless steel cutlery, surgical scalpels and tools, and in 1963 the first stainless steel razor blades were produced\(^3,4\). Table 1-1 summarizes the major ascents in the history of the development of stainless steel.
Table 1.1: Stainless steel development milestones

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1912</td>
<td>English metallurgist Harry Brearley invents stainless steel in his search for an alloy to protect cannon bores from erosion. The first commercial production of stainless steel occurs in August, 1913.</td>
</tr>
<tr>
<td>1915</td>
<td>During World War I, stainless steel is used to manufacture valves for aircraft engines.</td>
</tr>
<tr>
<td>1919-1923</td>
<td>Sheffield cutlers start regular production of stainless steel cutlery, surgical scalpels and tools.</td>
</tr>
<tr>
<td>1924</td>
<td>The first stainless steel roof makes an appearance in America.</td>
</tr>
<tr>
<td>1928</td>
<td>The brewery industry installs the first stainless steel fermenting tank.</td>
</tr>
<tr>
<td>1929</td>
<td>The first stainless steel tanker is used for transporting 3,000 gallons of milk.</td>
</tr>
<tr>
<td>1929-1930</td>
<td>The Chrysler Building’s top seven arches are clad in stainless steel. This New York City landmark is one of the world’s most recognized skyscrapers.</td>
</tr>
<tr>
<td>1931</td>
<td>The first stainless steel railway carriage appears in the US. Also, Rolls Royce produces the first stainless steel radiator grill and emblem.</td>
</tr>
<tr>
<td>1933</td>
<td>Stainless steel kitchen sinks and furniture are introduced.</td>
</tr>
<tr>
<td>1950</td>
<td>Stainless steel is used with increasing frequency for car accessories.</td>
</tr>
<tr>
<td>1954</td>
<td>The first stainless steel underwater TV camera is made.</td>
</tr>
<tr>
<td>1963</td>
<td>The first stainless steel razor blades are produced.</td>
</tr>
</tbody>
</table>

Stainless steel is defined as an iron-carbon alloy with a minimum of 11.5 wt% chromium content.
Its unique advantage over carbon steel is its high resistance to corrosion. This resistance to corrosion is due to the naturally occurring chromium-rich oxide film (Cr₂O₃) formed on the surface of the steel when exposed to oxygen. This oxide film, which forms at the molecular level, is extremely thin, around 2 nm, and is transparent. The oxide film protects the underlying steel from further reaction with the environment.

In order for stainless steel to be used in cutting applications, the hardness and the wear resistance are also important. To date, five categories of stainless steels were developed and commercialized, namely ferritic stainless steels, austenitic stainless steels, martensitic stainless steels, duplex stainless steels and precipitation hardened stainless steels. Martensitic stainless steels are widely used in cutting applications due to its hardenability, corrosion resistance and relatively low cost in comparison with other duplex stainless steels.
1.2 The processes of making high quality cutting instruments using martensitic stainless steel

The Cutlery or knife industry was not able to simply use stainless steel for cutting applications as it was invented. The first stainless steel did not produce knives that held an edge nor could edges be put onto blades easily. It took almost 30 years of expensive research by large cutlery manufacturers to develop the right compositions of alloys to produce the grade(s) of stainless steel that are still used today.

The typical process of making cutting instrument is that a certain grade of martensitic stainless steel is prepared at a steel mill. The steel is delivered in strip format. The strip is then hardened and sharpened. In some cases, edge hard coatings and or lubricious coatings are applied for superior performance of the cutting edge.

The hardening heat treatment of martensitic stainless steel is basically similar to the hardening heat treatment of carbon steels, involving three steps, austenitization, quenching, and tempering, but in a slower manner. This is because that 1) the secondary carbide dissolution in stainless steel is slower than the cementite carbide dissolution due to the presence of chromium and 2) the thermal conductivity of stainless steel is much smaller than that of carbon steel. In order to deliver hard, sharp and durable cutting instrument, the type of the martensitic stainless steel and the hardening heat treatment process are essential.

Sometimes the same grade martensitic stainless steel can be purchased from different suppliers, but can behave differently in the cutting tool manufacturing processes due to the
differences in steel manufacturing procedures among the producers. Often the question arises as to what are the key material characteristics that could impact the steel performance during the knife making process. Experimental evidence showed that the secondary carbide size distribution of the stainless has significant impact not only to the cutting product performance, but also to the cutting product manufacturing process performance, such process through-put, tool wear which can affect production maintenance cost.

It is well understood that the rate of carbide dissolution in martensitic steels is of primarily importance in the heat treatment process. However, relatively few studies on the rate-controlling mechanism have been carried out. It is quite common, in the industrial companies, to obtain the technical information from experiment without knowing the mechanism involved.
1.3 Research objectives and strategies

In order to thoroughly understand the materials, a detailed characterization has to be carried out, such as material chemical composition analysis, microstructure analysis, surface morphology, mechanical properties and secondary carbide particle type and size distribution analysis as well as their impact to the material properties, product performances.

The evaluation of the as-purchased steels with respect to their response to manufacturing can be achieved by comparing their microstructures at key steps of the manufacturing process. For this purpose, the dissolution and coarsening of secondary carbide was chosen as the primary material parameter in this research as it directly relates to the hardening and the retention of residual austenite which affects the manufacturability, as well as the performance of the products. To this end, a hardening test matrix can be carried out by varying austenitization temperature, austenitization time and tempering temperature, and then systematic quantitative metallographic measurements of carbide volume fraction can be conducted. The secondary carbide distribution of before hardening and after various hardening setting can also be determined.

An important element of this work was to develop a computer simulation model that predicts the dissolution and coarsening of secondary carbide particles during the hardening treatment. Using this model, the mechanical properties, such as strength and hardness, toughness of the material can be further predicated. The uniqueness of the model is that the secondary carbide dissolution and coarsening are considered simultaneously. Using the experimental data from the hardening test matrix and secondary carbide distribution analysis, the mathematic model of the secondary carbide dissolution and coarsening can be verified.
2. Theories

Martensitic stainless steels are a class of stainless steels with hardenability, meaning that the mechanical properties of the steels can be considerably altered by hardening heat treatment to achieve the desired mechanical properties, such as high hardness and high toughness etc. The typical heat treatments consist of austenitization at a temperature suitable for ferrite to austenite phase transformation and dissolution of carbides and then quenching for the hard martensitic phase to form. Precipitation hardening and tempering are sometime added to achieve even higher hardness and better toughness.

The material of interest for this study is a martensitic stainless steel containing 13% of chromium and 0.7% of carbon in a thin strip format. It is non AISI standard material, but is very popular for knife and cutlery applications today due to its excellent hardenability, very fine secondary carbide distribution and good corrosion resistance and relatively low cost. It also gives great ease of sharpening, ease in grinding and polishing and great wear resistance.

Unlike most AISI 400 series stainless steels, 0.7%C, 13%Cr steel has limited information available in the handbooks or test books due to its non standard material grade. The physical metallurgy of this material, its hardening heat treatment process as well as the kinetic theories about secondary phase dissolution and coarsening were visited through literature survey in this study.
2.1 Physical metallurgy of 13%Cr martensitic stainless steels

The major alloy elements of martensitic stainless steels are C, Fe, and Cr. AISI 400 series stainless steels represent typical martensitic stainless steels with compositions covering 12 – 18 wt. % Cr and 0.1 – 1.2 wt. % C which put the steels within the $\gamma$ (austenite) loop during austenitization as shown at the left center in Figures 2.1 and 2.2 and thus allowing them to undergo martensite transformation upon cooling to become hard steels during hardening heat treatment. Carbon is an element that is essential to changing iron into steel. Carbon adds hardness to steel through producing hard martensite. The higher the carbon content, the harder the martensite. Chromium provides steel with resistance to corrosion through producing a passive film of $\text{Cr}_2\text{O}_3$ on the steel surface. Sometimes, Mo, V and W are also added to achieve better corrosion resistance and high hardness. The other elements, such as Si, Mn, P, and S, are naturally existing or added to expand the range of material properties.

As the figure 2.1 shown for the alloy of iron and chromium, the field of the $\gamma$ loop is limited in size and the field of $\alpha$ ferrite is relatively large. Only iron-chromium alloys with less than 12-13% Cr undergo the $\gamma$ austenite to $\alpha$ ferrite transformation. With addition of carbon to iron-chromium alloys, the area of the gamma ($\gamma$) loop enlarges as shown in the figure 2.2 which are vertical sections through the Cr-Fe-C ternary diagram at 0.05%C, and 0.4% C respectively. The austenitic boundary increases to a maximum of 18% Cr with 0.4% C. The addition of C not only expands Gamma loop, but carbon also forms chromium carbides.
Figure 2.1: Fe-Cr equilibrium phase diagram without carbon content.

Figure 2.2: Fe-Cr vertical section of Cr-Fe-C ternary phase diagram at 0.05C wt % and 0.4C wt%.
The element chromium has a stronger affinity to carbon than iron and forms complex carbides containing both iron and chromium and it can form a whole series of different carbides with carbon and they have different crystal structures with formulae \( M_{23}C_6 \) and \( M_7C_3 \) where \( M \) represents the mixture of Fe and Cr. \( M_{23}C_6 \) and \( M_7C_3 \) are commonly referred as \( K_1 \) and \( K_2 \) respectively. The Cr:Fe atomic ratio can vary but total number of metal atoms cannot exceed 7 or 23. Examples of complex Fe-Cr carbide \( M_{23}C_6 \) can be \((\text{Cr}_{10}\text{Fe}_{13})C_6\), \((\text{Cr}_{18}\text{Fe}_{5})C_6\), and or \((\text{Cr}_{23})C_6\). Examples of complex Fe-Cr carbide \( M_7C_3 \) can be \((\text{Cr}_4\text{Fe}_3)C_3\), \((\text{Cr}_6\text{Fe})C_3\) and or \((\text{Cr}_7)C_3\). It was reported that \( M_7C_3 \) carbide has hardness of 79 Rc, compared to 72 Rc for the \( M_{23}C_6 \) carbide. Chromium reduces the size of the austenite phase field. Consequently much higher temperature is required for the steel to be austenitized and to dissolve the carbides.

The martensitic stainless steel used in this study has a unique chemical composition: 0.7% carbon, 13% chromium, the balance being iron and approximately 1% of the combined Mn, S, P and Ni. Of these alloying elements, C and Cr are the most critical ones in the martensitic stainless steels for knife and cutlery applications as the steel must provide good hardening and edge forming abilities.

In order to understand the properties of the stainless steel and the associated phenomena that take place in the knife making process, knowledge of the phase diagrams that relate to the alloying elements used in this steel are required. Many literatures had been reviewed. Figure 2.3 shows the phase diagram of 0.7% C, 13% Cr stainless steel calculated with Thermo-Calc®, coupled with PTERN thermodynamic database. The equilibrium values for solidus and liquidus temperatures were calculated to be 1734 K and 1652 K, respectively. In the
temperature range of 1417 - 1652 K, the microstructure of this stainless steel consists of just one single phase: austenite. At the austenitization temperature of, say 1325 K, the equilibrium amount of chromium-rich M₇C₃ carbides is 3.3 molar percent (2.6 volume percent). The equilibrium amount of carbon and chromium in the austenitic matrix at 1325 K is 0.44 wt. % and 11.4 wt. %, respectively. The amount of carbon and chromium in the matrix is a good indicator of the steel's hardenability and corrosion resistance. The equilibrium value for A₁ temperature (eutectoid temperature) was calculated to be 1087 K where ferrite matrix is transforming into austenite during heating. Under equilibrium conditions the austenite in 0.7%C, 13%Cr stainless steel transforms into ferrite or vice versa at this temperature.

Figure 2.3: Phase diagram of 13% Cr stainless steel of calculated with ThermoCalc®17, coupled with PTERN thermodynamic database. Si and Mn were excluded from the thermodynamic calculation.

The characteristics of the metallurgical structures of each phase in stainless steel are
tabulated in the table 2.1. Figure 2.3, 2.4, and 2.5 are schematic drawing showing the BCC, FCC and BCT respectively.

Table 2.1 Metallurgical Type and Structures

<table>
<thead>
<tr>
<th>Metallurgical Type</th>
<th>Phase Name</th>
<th>Crystal Type</th>
<th>No. of Atoms/unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrite</td>
<td>Alpha (α)</td>
<td>Body-Centered Cubic</td>
<td>9</td>
</tr>
<tr>
<td>Austenite</td>
<td>Gamma (γ)</td>
<td>Face-Centered Cubic</td>
<td>14</td>
</tr>
<tr>
<td>Martensitic</td>
<td>Quenched or tempered martensite</td>
<td>Distorted Body-Centered Tetragonal</td>
<td>10-13</td>
</tr>
</tbody>
</table>

Figure 2.4: Body centered cubic (BCC) structure.
Phase diagrams, describing the thermodynamic equilibrium of different alloys, show the equilibrium properties of the actual steels. Thermodynamic equilibrium requires, however, infinite slow cooling rate. In practice, during steel hardening heat treatment the maintenance of the thermodynamic equilibrium during cooling is neither possible nor desired. When a martensitic
stainless steel is heated from room temperature to the austenitization temperature at 1373 K, the phase diagram predicts several structural changes. For example, at approximately 1000 K, the ferrite transforms to austenite and M$_{23}$C$_6$ dissolves and at approximately 1100K, M$_7$C$_3$ starts to precipitate. If this steel is hardened from an austenitization temperature that is higher than 1417 K, the resulting martensitic microstructure will contain no carbides. In reality, this was not what had happened. The reason for this is that structural changes require diffusion of atoms, which is a time- and temperature dependent process. If the alloy is sufficiently super heated, the alloy may transform to metastable phases not predicted by the phase diagrams.

The microstructures of the martensitic stainless steels are principally determined by their chromium and carbon content and by the heat treatment. As can be seen from the phase diagram in figure 2.3, the steel used in this study contains a matrix of ferrite with randomly dispersed M$_{23}$C$_6$ carbides in as annealed condition at the room temperature. Due to the particular chemical composition of the steel used in this study, this steel lies almost on the carbon saturation line, which means that almost all of the carbides present in the austenitized and quenched state are precipitated carbides, not primary carbides. There is more carbon and chromium solutionized in the matrix. Thus the steel has excellent mechanical properties.

A very important characteristics of this steel is that it must have, in the as-received state, a very fine ferrite plus carbide structure so that, upon austenitizing, carbide particles dissolve quickly and uniformly in to the austenite, which then produces a martensite with controlled hardness and a fine distribution of un-dissolved carbide particles. Such a fine micro-structure is essential for giving the steel excellent hardness, toughness, great ease of sharpening, ease in grinding and
polishing, great wear resistance, and a very keen edge to a knife due to the absence of coarse secondary carbide particles.

Another importance feature of these steels is that the martensitic start temperature ($M_s$) must be above the room temperature. More precisely, the range of $M_s - M_f$ needs to be above room temperature to ensure a fully martensitic structure. Cutlery, surgical instruments, etc. are the common applications of such martensitic stainless steels.
2.2 Hardenability of martensitic stainless steels

As we know, carbon adds hardness to steel. The hardenability of steel is about the various solubility of carbon in the two allotropic forms of iron: 1) body centered cubic (BCC) and 2) face centered cubic (FCC). Below 900°C, the BCC form, known as ferrite or α-phase, exists and the solubility of carbon for α phase is 0.02%; while the FCC form, known as austenite or γ phase, exists between 900 and 1400°C and has solubility of carbon of 2.08%\(^\text{19}\). With very limited solubility in the BCC ferrite phase, the carbon, presented in the steel, forms carbides with iron or other alloy elements. Thus, the normal stable structure of the steel at room temperature would consist of two phases: α BCC iron and the carbides. On the other hand, carbon is very soluble in the γ FCC phase of iron (up to 2.08%). Thus, if the steel is heated to a temperature sufficient to cause transformation from α phase to the γ or austenite phase, the carbides dissolve. The more carbon diffuses into γ austenite phase, the harder the martensite will be. In order to achieve the maximum hardness of steel, martensitic transformation has to occur. The hardening heat treatment is the process where the transformation happens. It involves austenitization, quenching, sub-zero quenching, and precipitation hardening.

2.2.1 Austenitization

By definition, austenitization is a process to heat and hold the steel to a temperature at which it changes crystal structure from initial ferrite (BCC) to austenite (FCC) and simultaneously carbides start to dissolve into austenite solution. It is governed by the diffusion-controlled dissolution of the carbide into the austenite. Hence it requires heating the steel at a high enough temperature for a certain amount of time for the carbon to diffuse from the carbides to the austenite
matrix. The diffusion coefficient of a species increases exponentially with temperature. For example, the diffusion coefficient of carbon in austenite is doubled for a temperature rise from 1100 °C to 1180 °C. That is the same effect as that of doubling the time. Thus, temperature has much stronger effects than time on the distance of diffusion. In the case of chromium, the diffusion of Cr is much slower than that of C as Cr is a substitutional element in the austenite, while C is an interstitial element. For a given time at 1050 °C, the average C diffusion distance will be approximately 140 times greater than that of Cr. Thus, the rate of austenitization is limited by the substitutional diffusion-limited dissolution of these carbides. The carbides dissolution is limited primarily by the diffusion of Cr in the austenite. To speed up the homogenization process, one can increase the heat rate and the temperature. However, rapid heat or higher temperature holding can risk the material dimension stability resulting distortion or cracks and in some case austenite grain growth. Therefore the austenitization temperature, holding time and heating rate have to be properly selected. Also the proper gas media to ensure the heat transfer is also important.

Controlling particle size distribution is a critical issue in the commercial heat treatment of a particle containing alloy as the particle size directly affects to the performance of the heat treated alloy. Particle size is also linked to the amount of particle dissolution into the matrix that determines the mechanical properties of the heat-treated alloy, as in the hardening of a hypereutectoid steel. Thus, heating schedule must be optimized to obtain sufficient particle dissolution, i.e., solutionizing, while minimizing particle coarsening. Traditionally, this is achieved by experimentally adjusting the holding temperature and time for optimal microstructure and properties. While such an empirical method has often proven satisfactory in practice, it does have limitations, particularly when applied to a continuous heat-treating process, as the dissolution and
coarsening of second phase particles may progress even during the heating of the alloy to the holding temperature.

2.2.2 Quenching and sub-zero quenching

Quenching is a process followed by austenitization and it cools the heated steel down below martensitic start temperature ($M_s$) in a very fast manner, and martensitic transformation occurs.

The martensite, named after the German metallurgist Adolf Martens (1850–1914) is a hard phase and has a body centered tetragonal structure (BCT) which is a distorted BCC structure because of the excess carbon atoms held in solution as the figure 2.6 shows. The cubic cell contracts slightly along the $a$-axis, and $b$-axis; while expands greatly along the $c$-axis. The degree of the distortion increases with increasing carbon in solution. The increased distortion of the lattice leads to increased hardness.

As demonstrated by the Time-Temperature-Transformation (TTT) diagram as shown in figure 2.7, during the cooling from the austenitization temperature, many different phases can occur if the cooling rate is not fast enough. Among all the phases, such as austenite and pearlite, martensite has the highest hardness. In order to form martensite as much as possible to archive highest hardness of the steel and suppress the diffusional decomposition of the austenite, a certain cooling rate is required according the TTT of the steel. Fortunately for the Cr contained steels, the austenite and pearlite “nose” moves to higher temperature and longer times in the TTT diagram as shown in the figure of 2.7. The quenching can be carried out slowly in the air while still maintaining enough cooling rate for the martensitic transformation to occur.
Another important factor is that to cause martensitic transformation, the austenite must be cooled below the martensitic start temperature ($M_s$) rapidly. The $M_s$ depends on the chemical composition of the steel. In the martensitic transformation, the amount of austenite transformed to martensite purely depends upon the degree of super cool below the $M_s$ temperature. Complete transformation to martensite will be achieved when the temperature has fallen to the martensitic finish temperature ($M_f$). $M_s$ and $M_f$ are both depressed especially by increasing carbon content in solution, but also to a less extent by the presence of other alloying elements that stabilize austenite.
Often refrigeration is used to lower the final quench temperature and maximize the amount of martensite transformation. $M_f$ is rarely reached in alloy steels and a portion of the austenite remains untransformed as retained austenite (RA). Because of the depression of $M_s$ and $M_f$ temperatures, in high carbon and or alloyed martensite, the retained austenite increases with increasing carbon in solution for a constant final quenching temperature. Thus, measuring the retained austenite content at constant quenching temperature should indirectly indicate the degree of carbide dissolution.

The overall hardness will depend upon the relative proportions of hard martensite and soft retained austenite. The hardness of the martensite depends upon its carbon content. Because both $M_s$ and $M_f$ are depressed as carbide dissolution in austenite increases, the retained austenite will also increase. Thus, for a constant final quenching temperature, the steel hardness would at first increase with increasing carbide dissolution and then decreases as the retained austenite increases.

It is possible to dissolve all the carbides and form FCC austenite as the single phase in the steel. Slow cooling of the austenite from the higher temperature will then cause precipitation of the carbide again in the pearlitic structure. However, rapid cooling or quenching allows the austenite transform to martensite.

Martensitic transformation is diffusionless and occurs by the collective displacement of atoms as the austenite is sheared and expanded into martensite. As the transformation requires no individual jumps of atoms (i.e., no diffusion), it proceeds at a high rate (comparable to sound speed) even at low temperatures where diffusion is insignificant. Also, a large chemical driving force becomes available at low transformation temperatures.
Since no diffusion is involved in martensitic transformation, its product phase (martensitic) necessarily has the same chemical composition as that of the parent phase (austenite). Morphologically, martensite appears either lath-like or plate-like, depending primarily on its carbon content of the martensite. Low to medium carbon martensite normally has a lath-like morphology and hence is called lath martensite, while high carbon martensite has plate-like morphology, or mixture of tow. This is because the M_s temperature decreases with increasing carbon content, allowing the martensite to form in low-to-medium carbon steels at relatively high temperature in dislocated-lath morphology. High carbon martensite normally has plate morphology and hence called plate martensite. Plate martensite is characterized by the occurrence of micro twins within the martensite plate that reflect the lattice invariant transformation shear by twinning. In general, lath martensite is associated with high toughness and ductility, but low strength, while plate martensite structures are much higher strength but low in ductility.

The slower diffusion of chromium has no effect on martensitic transformation due to its diffusionless nature. However, chromium depresses the Ms and Mf temperature. Therefore, sub-zero treatment at -70°C is necessary to transform more austenite.

### 2.2.3 Precipitation hardening and tempering

Tempering the hardened steel at about 250 °C facilitates precipitation of the very fine ε-carbides together with restoration of the normal undistorted BCC structure and results in the hardness increase.

Cutting tools are sometimes tempered at about 350°C to achieve certain toughness with decrease of the hardness. This is because the carbide precipitation and lowered the carbon content
in the martensite.

The hardness of the tempered steel is directly related to the hardness of the as-quenched steel which depends upon the amount of C taken into solution, and thus principally upon the temperature at the time of austenitization. For the same amount of retained austenite, the higher the austenitization temperature, the higher the tempered hardness. Thus, the final hardness of the edge and the body of the sintered razor blade will be directly related to the austenitization temperature reached in the hardening furnace.
2.3 Kinetics of hardening heat treatment

The mechanical properties of a hardened stainless steel are decisively influenced by the hardening heat treatments, specifically by the carbide dissolution. The amount of carbon in the quenched martensite phase as well as the amount of un-dissolved carbide in the martensite exert an important influence on the characteristic properties of these materials, such as hardness, corrosion resistance, abrasion, and wear resistance. The rate of the hardening heat treatment or the rate of carbide dissolution for achieving the desired properties has direct impact to the productivity. Therefore a thorough understanding of the reactions taking place during hardening and the kinetics of the carbide dissolution is crucial for developing a mathematical model for predicting the mechanical properties of hardened steels.

2.3.1 Diffusion controlled secondary carbide dissolution

Unlike the subject of precipitate growth, carbide dissolution is not commonly described in the text books. Although both precipitate growth and dissolution are about diffusional mass movement, they are not simply the reverse of each other\textsuperscript{21}.

Through the literature search, it was found that, back in 1928, Hultgren\textsuperscript{22, 23} had started to study the gradual growth of austenite and the disappearance of ferrite by the same isothermal method and found that part of the cementite, originally present in the steel together with ferrite, did not dissolve at the same time as the ferrite disappeared but could be partly or completely dissolved on longer holding times at constant temperature. Hultgren suggested that the lower dissolution rate of the cementite might be caused by alloy elements, particularly the elements that are associated with cementite, because they would have to diffuse into the austenite as the cementite is being
dissolved. Two different mechanisms for carbide dissolution were discussed in the literatures in 70’s. One addresses the control of the carbide dissolution by an interface reaction while the other considers the diffusion in the austenitic as the rate-limiting step. The idea of an interface reaction controlling the dissolution of cementite in austenite is favored by Molinder\textsuperscript{24} in his studies of the austenitization behavior of chromium steel in soft annealed condition. Judd and Paxton\textsuperscript{25} found that the dissolution of cementite in a plain carbon steel could be well described using a diffusion model. However, the diffusion model was less successful in explaining the lower dissolution rate of the cementite. Nilsson\textsuperscript{26} concluded that the effect of the alloy element could be accounted for in a quantitative way by assuming complete diffusional control. Hillert\textsuperscript{27} pointed out that the possibility of local equilibriums at the phase interfaces. Later Hillert et al\textsuperscript{28} systematize the different mechanisms of dissolving cementite in austenite by 5 types of reactions. According to Hillert, the steel used in this study belongs to the reaction Type V, that is, the ferritic matrix transforms very rapidly to austenite, the carbide dissolution process occurring in three stages: stage 1 corresponds to the redistribution of carbon in the matrix connected with the beginning of carbide dissolution, during stage 2, the higher alloy content in the carbide at the carbide/matrix interface is leveled by diffusion towards the center of the carbide. The corresponding leveling in the austenite takes place during state 3. The reactions in all three stages are governed by diffusion. This model was tested, confirmed and is widely used nowadays\textsuperscript{29, 30}.

Since it is diffusion controlled dissolution, Fick’s first law can be applied. For the isothermal carbide dissolution in a Fe-Cr-C ternary alloy, it would be necessary to satisfy two mass balance equations:
\[(C_1^{\theta \gamma} - C_1^{\gamma \theta}) \nu = -D_1 \nabla \] (2.1)

\[(C_2^{\theta \gamma} - C_2^{\gamma \theta}) \nu = -D_2 \nabla \] (2.2)

where the subscripts refer to the solutes (1 for carbon and 2 for Cr), and \( \nu \) is the interface velocity \( = \partial z^*/\partial t \). Because the diffusivity of carbon atoms is much higher than the diffusivity of chromium atoms, these equations cannot in general be simultaneously satisfied for the equilibrium tie-line passing through the alloy composition \( C_1 \) and \( C_2 \). However, there are many tie-lines between the austenite and the carbide that apply with local equilibrium conditions at the austenite-carbide interface during carbide resolution.

When an alloy containing dispersed particles of secondary phases is raised above the solvus temperature of the precipitate, dissolution of the particles takes place under the chemical driving force arising from their thermodynamic instability at the higher temperature. During the particle dissolution, the concentration of the solute at far-field positions for the particle/matrix interface will remain unchanged, while that at the particle interface will be kept at the equilibrium value. Under such complex concentration profiles, it is not possible to find an analytical model to solve this problem of the volume diffusion controlled dissolution of a single phase. For simplicity, a few assumptions have to be made, such as, the concentration as \( r >> R(t) \) is assumed to be constant in this study. Its dissolution rate is determined by the thermodynamics and the kinetics of diffusion of the solute atoms.

At the interface between the austenite (matrix) and the carbide (precipitate phase), the structure and the composition change discontinuously. These discontinuities are maintained during
the migration of the interface, which constitutes growth or dissolution of the precipitate phase. Unlike the diffusionless transformations, such as martensitic transformation, occur without a compositional change, most diffusional transformations require long-range diffusion for the partitioning of alloy elements between the parent and product phases. The velocity of interfacial motion then depends on the diffusion of the atoms in the matrix and the rate of atomic transfer across the interface. In diffusion controlled interface migration, the former limits the rate, whereas in interface-controlled interface migration, the latter limits the rate.

Consider the dissolution of $K_1$ and $K_2$ carbides from the matrix of austenite. Mass balance must be satisfied for each element at the $K_1/\gamma$ and $K_2/\gamma$ interface. Zener\textsuperscript{31} presented the classical solution for a binary system using the following assumptions:

a) The dissolution rate is controlled by the diffusion of the solute, Cr in this case, in the matrix (austenite).

b) The dissolving particles are assumed to be spherical.

c) The concentration profile of the solute in the matrix at the interface of a particle of radius $r$ at any temperature during heating or holding is the same as the one that would be obtained by allowing the particle to dissolve isothermally to the radius $(r)$.

d) For simplicity, we adopt Zener’s linear approximation for the concentration profile which is defined by the tie-line concentration $C_{Cr}^\gamma$ of the austenite and $C_{Cr}^\infty$ the far-field concentration and the global mass balance.

e) No impingement of diffusion zones of adjacent particles is considered. (A long-time treatment could account for diffusion-zone impingement).
2.3.2 Particle coarsening: Ostwald ripening

During the heating of an alloy consisting of a matrix phase (solid solution) and second phase particles such as in martensitic stainless steel, the second phase particles dissolve into the matrix as the solubility of the second phase increases with increasing temperature. The particle dissolution may also be accompanied by particle coarsening which is driven by the energy of the particle-matrix interface\textsuperscript{32, 33}. This is because that the microstructure of a two-phase alloy is always unstable if the total interfacial free energy is not minimized. Thus, the second phase particles in a heat-treated alloy have a size distribution that depends on the kinetics of not only dissolution but also coarsening.

As mentioned earlier, it was evident experimentally that hardening heat treatment dissolves carbide and reduces the total volume fraction of the secondary carbide and the carbide density, but the mean diameters of the carbides are remained almost unchanged or sometimes even increased. It was believed that Ostwald ripening had to be taken into consideration. Ostwald ripening is such that small particles shrink and dissolve, while large particles grow the spare of small particles.

In any precipitation-hardened specimen there will be a range of particle sizes due to differences in nucleation time and growth rate. Due to Gibbs-Thomson effects, the solute concentration in the matrix adjacent to a particle will increase as the radius of curvature decreases, which will cause the solute to diffuse away from the smaller particles in the direction of the larger particles, so that small particles shrink and disappear while large particles coarsen. The overall result is that the total number of particles decreases and the mean radius increases with time. By assuming that the volume diffusion is the rate controlling step, it has been shown that the following
relationship should be obeyed:

\[ \bar{r}^3 - \bar{r}_o^3 = k \cdot t \]  

(2.3)

where \( k = \frac{C \cdot D \cdot \gamma \cdot X_e}{R \cdot T} \), \( \bar{r}_o \) is the mean radius at time \( t=0 \), \( D \) is the diffusion coefficient, \( \gamma \) is the interfacial energy, \( X_e \) is the equilibrium solubility of the particles and \( C \) is a numerical constant. The rigorous LSW\textsuperscript{34,35,36} analysis resulted \( C \) equals \( \frac{8}{9} \). Since \( D \) and \( X_e \) increase exponentially with temperature, the rate of coarsening will increase rapidly with increasing temperature. Therefore,

\[ \frac{dr}{dt} \propto \frac{k}{r^2} \]  

(2.4)

Nevertheless, often secondary carbide dissolution and coarsening were considered separately. In the study, simulation model was developed by treating both effects simultaneously. The Lifshitz-Slyozov-Wagner (LSW)’s equation was applied in this study.
3. Experimental Procedures

The experiments were carried out and the test matrices were designed in order to understand the carbide dissolution and coarsening during the austenitizing of the martensitic stainless steels. This includes verifying chemical composition, analyzing the surface morphology, identifying and verifying the carbide phases in the steel matrix, measuring mechanical properties such as hardness and the amount of retained austenite. The hardening heat treatment matrix was carried out by varying austenitization temperature and austenitization time. Lastly the secondary carbide size distribution was characterized using the specimen from the hardening treatment matrix to obtain the data to verify the simulation model.
3.1 Material characterization

3.1.1 Chemical composition of the material of interest

The chemical composition of the steel was performed by inductively coupled plasma/optical emission spectrometer. Carbon and sulfur were performed by Leco combustion method. The chemical composition for this study was performed in a commercial laboratory with certified results.

3.1.2 Surface characterization by scanning electron microscopy (SEM)

The steel of interests has very smooth surface finish; and the surface morphology is not easily been discernible by optical microscope or numerically measured. In this study, Hitachi S4200 Field Emission Scanning Electron Microscope was used to record and compare the difference of the surface feature of the steels.

Table 3.1: SEM settings for surface morphology analysis

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Acceleration voltage</strong></td>
<td>15- 25 KV</td>
</tr>
<tr>
<td><strong>Beam current</strong> 10</td>
<td>10+ μAmp</td>
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<tr>
<td><strong>Working distance</strong></td>
<td>15 – 20 mm</td>
</tr>
<tr>
<td><strong>Magnification</strong></td>
<td>5000X</td>
</tr>
</tbody>
</table>

3.1.3 Phase analysis by X-ray diffraction (XRD)

X-ray diffraction was used to analyze secondary carbide phases. XRD analyses were
performed using D8 DISCOVER X-ray diffractometer with GADDS® (General Area Diffraction Detector System) introduced by Bruker AXS. The diffraction resolution has 7 degrees of freedom for sample handling: \( \theta \) \((\omega)\), 2\( \theta \), \( \phi \), \( \chi \), s, y, and z. Radiation Cr-K\( \alpha \) at 2.29Å in the 2\( \theta \) range from 47\(^\circ\) to 158\(^\circ\) was used. Steel sample was installed vertically in a magnetic holder in a vertical position \((\chi = 90^\circ)\). The sample to detector distance is set at 15 cm, which allows for the entire angular range coverage using four frames of 25\(^\circ\) apart. The spectra were then recorded and the peaks were characterized using standards in the data library.

3.1.4 Hardness by Vicker’s hardness tester

A Mitutoyo Micro Hardness Tester (MVK-H1) and a computer assisted measurement system were used to measure the hardness of the annealed strip and the hardened strip. A small piece of sample after polishing was placed on the Micro Hardness Tester, and was then indented for twelve seconds using a 300 g load for soft steel and 1 kg load for hardened steel. The indenter had a diamond pyramid shape and produced a diamond impression on the steel. The diamond image from the soft or hardened steel sample was projected by a digital camera to the monitor of the computer assisted measurement system. The computer assisted measurement system measured the hardness by determining the diagonal lengths of the diamond impression and then computing the Vickers Hardness Number (Hv).

3.1.5 Determination of Retained austenite

Amount of retained austenite after martensitic transformation is commonly measured by X-ray diffraction. However, it is not very practical for manufacturing practice. An alternate way is to obtain the martensite content by measuring the magnetic balance of the material and then the
retained austenite can be subtracted.

Martensite is magnetic and untransformed austenite is non magnetic. A ferromagnetic body in a non-uniform magnetic field, when saturated, experiences a force in the direction of the stronger part of the field, which is given by:

\[ F = m \sigma \frac{dH}{dx} \]  

(3.1)

where \( F \) = force (dynes), \( m \) = mass of body (grams), \( \sigma \) = saturation magnetic moment per unit mass of the body (c.g.s.) and \( \frac{dH}{dx} \) = field gradient (oersteds/cm). Magnetic balances are devices for measuring the force acting on a specimen in a non-uniform field. Non magnetic phases in the specimen reduce the effective mass of the specimen and alloying elements may affects saturation magnetic moment per unite mass of the body (\( \sigma \)). A magnetic balance can thus be used to determine the proportion of non-magnetic material, such as retained austenite in a ferromagnetic alloy whose magnetic properties are known. Since the un-dissolved carbides are non magnetic, Magnetic austenite determinator reads both retained austenite and un-dissolved carbide. Therefore, the amount of the retained austenite measured by the magnetic balances is different from that measured by XRD in value.
3.2 Hardening heat treatment and heat treatment equipment

Custom built inline heat treatment equipment is capable of austenitization, air-quenching; sub-zero quenching, and precipitation hardening. The furnace temperature is monitored by Ircon non-contact infrared pyrometers and thermal couples.

Figure 3.1: Schematic illustration of inline heat treatment process

3.2.1 Austenitization

The austenitization furnace consists of several heating zones with independent temperature controls. With known furnace length and strip feeding speed, the total nominal austenitization time can be determined and also can be varied by adjusting the strip feeding speed. The steel strip during austenitization is protected from oxidation by a H₂ and N₂ mixture gas.

The furnace design does not permit direct measurement of the steel temperature during the hardening process. It was assumed that the strip reached the same temperature of the furnace immediately since the specimen is very thin.

The furnace temperature profile was measured for each austenitization temperature setting.
In this operation, a thermocouple is inserted between the entrance of the furnace and the exit of the furnace and withdrawn at 6 inch interval to measure measurements at each position. Thus a temperature profile plot inside of the furnace tube can be constructed.

3.2.2 Quenching

The quenching was carried out in air inside a device. The device is water cooled. The temperature of the water is maintained at 35°C. The quench rate is not critical for 13%Cr blade steel.

3.2.3 Sub-zero quenching

Sub-zero treatment is carried out in a two feet long refrigeration freezer. The function of the refrigerator is to transform the retained austenite to martensite and thereby to increase the hardness of the steel. The refrigeration temperature was set at -75°C constant.

3.2.4 Tempering or precipitation hardening Furnace

The tempering furnace is a five feet long unit which tempers the strip in air. The strip temperature is not measured although the furnace temperature is set.

In the present study, the tempering furnace temperature was set in a way that precipitation can occur. Therefore the temperature of the tempering furnace is selected based on the maximum hardness that the material can reach.
3.3 Design of hardening experiment

In order to study the secondary carbide dissolution and coarsening, a hardening test matrix was designed to fulfill such possible studies.

Three furnace settings at 1110 °C, 1145 °C and 1175 °C were selected and three nominal austenitization ambient temperatures 1081 °C, 1114 °C, and 1143 °C were obtained. The furnace ambient temperature was lower than the furnace setting because the setting controls the outside of the furnace metal tube. The furnace ambient temperature was measured before the heat treatment test according to Section 3.2.1 in order to obtain the accurate austenitization temperature. It should be noted that the so-called nominal austenitization temperature is referring to the furnace ambient temperatures. The actual strip temperature was not a constant during the hardening treatment. It was consisted of three periods: 1) heating, 2) holding temperature at the setting temperature, and 3) cooling at the exit of the furnace.

At each austenitization temperature setting, four nominal austenitization times, 6 seconds, 7.5 seconds, 11.25 seconds and 18 seconds, were selected. The selected austenitization time was achieved by varying the steel strip moving speed. Again, it should be noted that the so-called nominal austenitization time is referring to the entire time while the strip is running through the austenitization furnace which includes heating, holding period at a temperature and cooling.

At each austenitization temperature and austenitization time setting, 7 different tempering (precipitation hardening) temperatures were also selected. Then the material properties, such hardness and the amount of retained austenite were analyzed and the secondary carbide was
characterized after the hardening tests. Tables 3.2 below summarize the test matrix.

Table 3.2: Design of hardening experiment design

<table>
<thead>
<tr>
<th>Austenitization Temperature (°C)</th>
<th>1081 (°C)*</th>
<th>1114 (°C)*</th>
<th>1143 (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austenitization Time (Seconds)</td>
<td>6.0</td>
<td>7.5</td>
<td>11.25</td>
</tr>
<tr>
<td>Precipitation temperature (°C)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>25</td>
<td>25</td>
<td>25</td>
</tr>
<tr>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>200</td>
<td>200</td>
<td>200</td>
<td>200</td>
</tr>
<tr>
<td>250</td>
<td>250</td>
<td>250</td>
<td>250</td>
</tr>
<tr>
<td>280</td>
<td>280</td>
<td>280</td>
<td>280</td>
</tr>
<tr>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>350</td>
<td>350</td>
<td>350</td>
<td>350</td>
</tr>
</tbody>
</table>

Note: * indicates nominal austenitization temperature
3.4 Secondary carbide Characterization

Characterizing carbides size distribution in steel is a very complex and difficult task. Historically, carbide analysis was carried out using the Koch Sunderman technique\textsuperscript{37}, or by wet chemistry method\textsuperscript{38,39,40}. According to the Koch-Sundermand technique, carbides are potentiostatically isolated from specimens in 1% HCl. The residues were weighed and analyzed for phase identification. Similarly, in wet chemical analysis, carbide particles are extracted from the steel. For example, a very small piece of steel samples, weighed accurately, is dissolved in 25 ml if 10% ammonium persulphate solution. The solution with dissolved steel sample is added to a filtrate. Then the carbide particle composition and size can be accurately measured by scanning electron microscope (SEM) and X-ray diffraction spectroscopy (XRD). Although it is extremely cumbersome and time consuming, this method is accurate and reproducible. S. Hahn et al\textsuperscript{37} used this method and compared the “true” carbide diameters which were measured by chemically extracting and isolating carbides using wet chemistry method to the “observed” carbide diameters which were from polished and etched steel samples and found that, numerically, the difference was within 6% and he concluded that it was close enough to estimate the “true” diameters distribution from the “observed” diameters. Hahn’s work had established an important foundation for measuring carbide size distribution using two dimensional computer assisted image analysis techniques. With the broad availability of electron microscopes, the two dimensional carbide analyses became popular. It involves preparing a metallographic sample and taking micrographs by optical microscope at 1000 magnification or by SEM at 5000 or higher magnification. Then the number of carbide particles can be manually counted from a micro structural photograph within the known area such as 10\(\mu\)m by 10\(\mu\)m. In this method, it only gave carbide density information, the
carbide size could be estimated, but could not be measured accurately.

In the present study, a technique combined with metallographic procedure, SEM and digital computer assisted image analysis was used. Secondary carbide size distribution in martensitic stainless steel in as-annealed state or as-hardened state can be revealed and each carbide particle can be measured, characterized, and compared to the different samples.

3.4.1 Metallography

An ASTM standard metallographic procedure was conducted. Sample preparation included, placing a small piece of steel specimen in longitudinal direction in a mounting vise, separating the steel specimen with nickel shims to help identify the samples if more than one sample is used. Castable (cold) mounting compounds with added conductive filler were used in this study. The scheme of the sample mount is shown in Figure 3.1. Once the mounted sample is consolidated, the mounted sample is ground and polished using standard metallographic procedure. The finished sample has surface smoothness 1 μm Ra or better.
Then, the polished sample is etched by fresh-made Murakami reagent for 60 seconds at the room temperature to reveal the secondary carbides. The Murakami reagent is listed in Table 3.3.

<table>
<thead>
<tr>
<th>Potassium Ferricyanide</th>
<th>K₃Fe(CN)₆</th>
<th>10 gm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium Hydroxide</td>
<td>KOH</td>
<td>10 gm</td>
</tr>
<tr>
<td>De ionized Water</td>
<td>H₂O</td>
<td>100 ml</td>
</tr>
</tbody>
</table>

The sample was then examined under an optical microscope to ensure the quality of the sample preparation for SEM imaging.

**3.4.2 SEM micrograph**
A Hitachi S4200 Field Emission Scanning Electron Microscope is used for secondary carbide analysis. Typical SEM settings for secondary carbide analysis are listed in Table 3.4. Care was taken to ensure the highest image quality in terms of particle resolution and focus, and images were saved in high resolution TIFF format.

Table 3.4: Scanning Electron Microscope operation settings

<table>
<thead>
<tr>
<th>Acceleration voltage</th>
<th>15- 25 KV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam current</td>
<td>10+ μAmp</td>
</tr>
<tr>
<td>Working distance</td>
<td>15 – 20 mm</td>
</tr>
<tr>
<td>Magnification</td>
<td>8000X</td>
</tr>
</tbody>
</table>

Figure 3.2 shows an SEM micrograph of the microstructure of a martensitic stainless steel in the as-received annealed condition at magnification of 8000X. The dark colored particles are the secondary carbides, $M_2\text{C}_6$, and the light colored background is the ferrite matrix. At such a high magnification, only a limited number of carbides were seen in each SEM micrographs, In order to assure statistical confidence, five images were taken from each specimen.
3.4.3 Quantitative image analysis

Quantitative image analysis was performed using the program ImagePro Plus V4.5 produced by Media Cybernetics. At first, the spatial calibration has to be set up based on the image magnification. The image analysis software relies on a series of reference images of known size to determine the actual size of the items on a picture. The scale bar of an SEM reference image at magnification of 8000 was used to teach the image analysis software to report micrometer units instead of pixels.

Figure 3.4 shows the first screen when an SEM image is loaded into the ImagePro Plus software. The dark colored particles are the carbides and the light colored background is ferrite matrix. The SEM image scale bar was intentionally removed for image analysis purpose, so it
would not be counted.

The next step was to select the region of interest. In this study, the entire SEM image is selected since the scale bar as well as other image information had already been excluded. Then image process is carried out. This is because that the SEM images typically do not have an even shade of the background nor the carbide particles. In order to remove the disturbing background, a median and Gauss filters were applied. Typical settings are *Lo Pass 7x7, Hi Gauss 7x7 and Median 7x7* depending on the SEM image quality. Figure 3.5 shows a view after the application of the filters. An image enhancement is further applied. It includes adjusting the image brightness and contrast. Care should be taken to ensure the original carbide size and shape are not altered. Figure
3.6 shows a view after application of image enhancement and the carbide particle and ferrite matrix background are much better evenly colored distinguished from each other.

Figure 3.5: View of a SEM image after applying the filters
Figure 3.6: View of a SEM image after applying image enhancement

With the processed image as shown in Figure 3.6, the threshold function can be applied. The function further separates the carbide particles of interest from the ferrite background and removes unwanted background information and leave behind only the particles which are displayed in red as the Figure 3.7 shows. By applying the “count” function, each particle in the image is then numbered.
Secondary carbides are often not perfectly uniformly distributed. In addition, the SEM images are seldom perfectly shaded for the threshold function to work. It can cause false particle counting. Therefore, additional image edit was conducted. Using ImagePro Plus, one can separate particle cluster by drawing lines across the particle. One can also draw a circle to merge a particle which was separated due to the uneven shade of the SEM image. For example, particle #42 and #43 in Figure 3.7 are actually one particle. By drawing a circle to close them up, they become one particle as numbered #39 shown in Figure 3.8. Particle #27 and 36 in Figure 3.8 are actually particle clusters as shown in Figure 3.7. By drawing a circle, they become one particle as shown in Figure 3.8. After that, by drawing lines to mimic the particle cluster, they become two particles as shown in Figure 3.9.
Figure 3.8: The particles were merged by Image Edit

Figure 3.9: articles were separated by Image Edit
Once the image is ready for analysis, one will have to select the measurements. There are many measurements one can select from ImagePro Plus in order to obtain carbide radii and carbide area fraction. For instance, one can select “Area” that measures area of each particle as the red area show in Figure 3.9. “PerArea” measures the ratio of area of a particle to the total area of an image or ROI, “Perimeter” measures the length of the particle’s outline, etc. The selected measurements can be exported to an Excel file, and the data from multiple images of a steel sample can be appended into one Excel file which permits statistical calculations of the data. Table 3.5 is an example of a typical image analysis output. The yellow shaded columns are calculated from the image analysis outputs, such as the “equivalent radius” is calculated by \( \sqrt{\frac{\text{Area}}{\pi}} \) and then \( \ln r \) can be calculated from the “Equivalent radius”. By adding up the “Per-Area”, the area fraction can be obtained. In this study, “Area” was selected for calculating carbide radii and subsequently \( \ln r \) for Gaussian distribution.

Table 3.5: Example of exported particle counts and selected measurement

<table>
<thead>
<tr>
<th>Obj#</th>
<th>Area</th>
<th>Perimeter</th>
<th>Per-Area</th>
<th>Equivalent Radius (Area)</th>
<th>Ln r</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.03392</td>
<td>0.87497</td>
<td>0.00020</td>
<td>0.10392</td>
<td>-2.26417</td>
</tr>
<tr>
<td>2</td>
<td>0.38599</td>
<td>2.65289</td>
<td>0.00231</td>
<td>0.35052</td>
<td>-1.04834</td>
</tr>
<tr>
<td>3</td>
<td>0.21735</td>
<td>22.69136</td>
<td>0.00130</td>
<td>0.26303</td>
<td>-1.33548</td>
</tr>
<tr>
<td>4</td>
<td>0.01755</td>
<td>0.56291</td>
<td>0.00011</td>
<td>0.07475</td>
<td>-2.59360</td>
</tr>
<tr>
<td>5</td>
<td>0.03649</td>
<td>0.83885</td>
<td>0.00022</td>
<td>0.10777</td>
<td>-2.22774</td>
</tr>
<tr>
<td>6</td>
<td>0.18284</td>
<td>1.76536</td>
<td>0.00109</td>
<td>0.24124</td>
<td>-1.42194</td>
</tr>
<tr>
<td>7</td>
<td>0.26765</td>
<td>2.04541</td>
<td>0.00160</td>
<td>0.29188</td>
<td>-1.23140</td>
</tr>
<tr>
<td>8</td>
<td>0.35700</td>
<td>2.36929</td>
<td>0.00214</td>
<td>0.33710</td>
<td>-1.08738</td>
</tr>
<tr>
<td>9</td>
<td>0.46607</td>
<td>2.57608</td>
<td>0.00279</td>
<td>0.38517</td>
<td>-0.95408</td>
</tr>
<tr>
<td>10</td>
<td>0.17179</td>
<td>1.56210</td>
<td>0.00103</td>
<td>0.23384</td>
<td>-1.45310</td>
</tr>
<tr>
<td>11</td>
<td>0.18008</td>
<td>2.05712</td>
<td>0.00108</td>
<td>0.23942</td>
<td>-1.42955</td>
</tr>
</tbody>
</table>
The image analysis outputs the planar “area” and the planar radii from a metallographic cross section. The radii obtained from the two dimensional image analyses are ≤ the maximum radius of a particle. This can create an error for the numerical calculations. Although the secondary carbides were spheroidized during the annealing process at the steel mills, often the secondary carbide particles of steel are not perfect spheres as can be seen from the above images. The precise shape of the particle size and their dispersion make the analysis a difficult job to achieve. For simplification, the ‘equivalent sphere” concept was used, which assuming all particles are spherical in nature. Then one can calculate the radii of all carbide particles as listed in Table 3.5 using the Eq. (3.2) and (3.3)

\[ A = \pi \cdot r^2 \]  \hspace{1cm} (3.2)

\[ r = \sqrt{\frac{A}{\pi}} \]  \hspace{1cm} (3.3)

where \( r \) is the radius of an equivalent sphere according to the equivalent sphere theory. This
ensures that we do not need to describe the actual shape, which can be quite difficult.

Lastly, the statistical calculations can be carried out. The entire carbide particle collection from multiple images was divided into 20 bins from 0 to 1 \( \mu \text{m} \) or the maximum carbide radius. The number of carbide particles fallen in each bin can be calculated and the histogram (a bar graph) and frequency curve (a “smooth-out histogram) can be plotted as Figure 3.10 shows as an example. A graph such as Figure 3.10 can be used to compare the steel subtle differences in secondary size carbide distribution.

![Figure 3.10: An example of carbide size distribution with different steel specimens](image)
4. Experimental results and discussions

Experiments conducted for this work includes characterizing the steels in the as-annealed condition, carrying out heat treatment tests, and quantitative analysis of secondary carbide size distribution based on the experimental procedures described in Section 3. The experimental results are presented and analyzed in this section.
4.1 Material characterization of as received steel sample

Two steel samples, A and B, of the same nominal composition of Fe - 0.7wt. % C-13wt. % Cr, were studied in this work. The two steel samples reflect two different manufacturing processes, such as different casting methods, different hot rolling techniques and different cold rolling reduction procedures. The material characterization was first conducted on the as-received samples. It included determining the chemical composition, and identifying carbide phases in the microstructure as well as evaluating the microstructure before and after the heat treatment.

4.1.1 Chemical composition

The chemical composition was analyzed in a commercial laboratory by Inductively Coupled Plasma/Optical Emission spectrometry. Carbon, sulfur, nitrogen, hydrogen and oxygen were determined by Leco Combustion method. As shown in Table 4.1, the two steels are nearly identical based on their chemical compositions.

<table>
<thead>
<tr>
<th>Elements (Wt. %)</th>
<th>C</th>
<th>Cr</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel A</td>
<td>0.69</td>
<td>12.62</td>
<td>0.66</td>
<td>0.35</td>
<td>0.035</td>
<td>0.001</td>
<td>0.11</td>
<td>Remainder</td>
</tr>
<tr>
<td>Steel B</td>
<td>0.70</td>
<td>13.05</td>
<td>0.76</td>
<td>0.28</td>
<td>0.036</td>
<td>0.001</td>
<td>0.09</td>
<td>Remainder</td>
</tr>
</tbody>
</table>

4.1.2 Surface morphology of the steel samples

Surface morphology is an important factor to distinguish materials from different suppliers as it is affected by cold rolling pressure, speed, lubricant as well as other Steel mill settings. The surface roughness of the steel is directly related to the surface morphology. Surface roughness
impacts steel heat treatment process because it affects emissivity and hence the effectiveness of heat exchange during the heat treatment. Because the surface finish of the steel is very smooth in macroscopical view, it is difficult to distinguish the difference in roughness quantitatively. In this study, SEM micrograph was taken at higher magnification of 5000X, and therefore the surface morphology can be compared qualitatively from steel to steel. Figures 4.1 and 4.2 are the surface morphology from Steel A and B. It appears that Steel B is slightly rougher than Steel A.

Figure 4.1: Surface morphology of Steel A.
4.1.3 Phase characterization by X-ray diffraction

The carbide phases present in the steel samples were identified by XRD for the as-received steels and as-hardened steels. Figures 4.3 and 4.4 show the X-ray diffraction patterns of Steels A and B in the as-received annealed condition, respectively. M$_{23}$C$_6$ and $\alpha$ ferrite were identified. The ferrite peaks were located at 2$\theta$s of 69°, 106.3° and 156.1° which correspond to the (110), (200), and (211) peaks, respectively, M$_{23}$C$_6$ peaks is located at a 2$\theta$ of 134° and 140°. In the hardened state, martensite, retained austenite and M$_{23}$C$_6$ were identified. Figure 4.5 shows the overlapped XRD spectra of hardened Steel A and B (Steel A is in pink color and Steel B is in Green color). The intensity and the position of the corresponding peaks are quite similar between the two soft steels as shown in the Figure 4.3 and 4.4 and two hardened steels as shown in the Figures 4.5 respectively. Omsen et al. reported$^{28}$ that a Fe-0.74 Wt %C -14 wt. %Cr steel, comparable to the
steel studied in this work, had 1% of $M_7C_3$ in the annealed state. Therefore, a detailed search for $M_3C_7$ on both annealed steels and hardened steels was also conducted. Figure 4.6 shows an XRD pattern of as-received steel B where no peaks of $M_7C_3$ are found (the red vertical lines are where the $M_7C_3$ peaks should be). Thus, $M7C3$ was not present in steel B in any significant amount. The same result was obtained from for Steel A.

Figure 4.3: XRD spectrum of steel A in as-annealed condition.
Figure 4.4: XRD spectrum of steel B in as annealed condition

Figure 4.5: Overlapped XRD spectra of steel sample of hardened Steel hardened steel A and steel B (Steel A is in pink) color and Steel B is in Green color
Based on analysis by XRD, there is no significant differences were noted between Steels A and B in terms micro structures.

### 4.1.4 Microstructure evaluation

The polished and etched samples were then examined under the optical microscope at 1000x magnification. Figures 4.7 and 4.8 are optical micrographs of the two martensitic stainless Steels A and B in the annealed condition. As indicated in the pictures below, the microstructure is composed of globular secondary carbide (M\textsubscript{23}C\textsubscript{6}) particles in the ferrite matrix. Visually there is no distinguishable difference in microstructure between steel A and Steel at magnification of 1000X.

To reveal the carbide particles at higher magnification, the as-received steels were investigated by SEM. Figures 4.9 to 4.10 show the respective microstructures. It is apparent that both steels exhibit virtually identical initial annealed microstructures where fine, well spheroidized...
secondary carbide particles are uniformly distributed in the ferrite matrix. No visible non metallic inclusion or defects were observed in either steel.

As one can see, both optical and SEM images give qualitative information about the microstructures, they cannot distinguish the subtle difference between the steels without quantitative analysis. Therefore, a quantitative image analysis is necessary for characterizing secondary carbides.

Figure 4.7: Optical microstructures of steel A at as-annealed at 1000x
Figure 4.8: Optical microstructures of steel B at as-annealed at 1000x

Figure 4.9: SEM micrograph of steel A at as-annealed at 5000X
Figure 4.10: SEM micrograph of steel B at as-annealed at 5000X
4.2 Results of the heat treatment experiment

The austenitization furnace ambient temperature profiles were measured prior to hardening treatment. They were obtained by measuring the temperature as described in Section 3.3 with strip running in the furnace. Figures 4.11 – 4.13 show the furnace temperature profiles for three nominal austenitization temperature settings, respectively. Since the steel austenitizing time was controlled by the strip feeding speed, the longer the austenitization time, the slower the feeding speed. The different strip feeding speed resulted in different heating rate as shown Figures 4.11-4.13. For example, the pink colored temperature profile represents the longest austenitizing time (18 s) and the slowest strip feeding speed, which resulted in the slowest heat rate when it entered the furnace.

Figure 4.11: Austenitization temperature profile for \( T=1081 \, ^\circ C \)
Figure 4.12: Austenitization temperature profile for T=1114°C

Figure 4.13: Austenitization temperature profile at T=1143°C
Once the austenitization furnace temperature profile was obtained, hardening experiments were carried out under a matrix of conditions. At each setting, the steel samples, A and B, went through austenitization, quenching at 35°C and deep quenching at -75°C, and then the hardness and the amount of retained austenite of each sample were measured. The Since Steel A and B showed the similar trends, only selected plots of hardness and amount of retained austenite are discussed below.

Figure 4.14 shows the hardness at various tempering temperature at three austenitization temperatures 1081°C, 1114°C, 1143°C, respectively. Tempering at T=25°C means no tempering was carried out; therefore its hardness represents that of the as-deep quenched condition. Reheating the steel after quenching and deep quenching causes precipitation hardening. At about 250 - 280°C, it reaches the maximum precipitation hardness regardless of the austenitization temperature. Therefore, the tempering temperature between 250 - 280°C in this case, is often selected as the best precipitation temperature for optimizing the hardening treatment. Upon increasing the tempering temperature beyond the 280°C, the hardness drops due to over tempering caused by the coarsening of tempered carbide particles. Higher resistance to over-tempering resulted in steels austenitized at higher temperatures as shown by the yellow curve in Figure 4.14. It is also noticed that austenitizing at 1114 °C gives higher precipitation hardness than austenitizing at 1081°C 1143°C.
Figure 4.14: Hardness as a function of tempering temperature at different austenitization temperatures at the selected austenitization time (7.5 s)

Figure 4.15 shows that, for a fixed nominal austenitization temperature, the amount of retained austenite does not change with tempering temperature. It is also noticed that, for a fixed nominal austenitization time, higher austenitization temperatures cause retention of more austenite. Thus, the amount of retained austenite is solely determined by the dissolution of secondary carbide during the austenitization, and tempering below 350°C has no effect on the decomposition of retained austenite.
At the selected nominal austenitizing time (e.g. 7.5 seconds), austenitizing at 1114°C gives the highest hardness as indicated in Figure 4.16. Thus, austenitizing below 1114°C causes insufficient carbide dissolution for the martensite to have sufficient hardness. Austenitizing above 1114°C allows more carbide to dissolve in the austenite, but this has an effect of stabilizing the austenite, merely increasing retained austenite in the hardened steel. This is because more carbon in the austenite solution increases martensite hardness, but also decreases the martensite starting temperature ($M_s$) and subsequently reduces the amount of martensite during cooling (martensitic transformation). Consequently the steel austenitized at 1143°C has a lower hardness than that of the steel austenitized at 1114°C. Figure 4.17 shows that the hardness after tempering at 250°C increases not only with increasing austenitization temperature but also with increasing...
austenitization time. This is because both austenitization temperature and time increase the amount of carbide dissolution which enriches the austenite with carbon, a strong austenite stabilizer. Figures 4.16 and 4.17 are useful for selecting the optimal austenitization temperature in order to obtain the peak hardness and to balance between creating hard martensite and retaining soft austenite.

Figure 4.16: As quenched Hardness vs. austenitization temperature at the selected austenitization time (7.5 Seconds) when tempered at 250 °C.
Figure 4.17: As quenched retained austenite vs. austenitization time at different austenitization temperature.

Figure 4.18 shows that the hardness of as-deep quenched steel increases with increasing austenitization time at 1081°C and 1114°C. Figure 4.16 also shows that the hardness increases rapidly initially due to the fast carbon diffusion into the austenite in the “stage 1” as described by Hillert et al\textsuperscript{12}. Further increases in austenitization time, chromium diffusing into the austenite matrix, causes a decrease of the $M_S$ temperature and hence an increasing in retained austenite. The later effect is more pronounced at higher austenitization temperatures, particularly at 1143°C.
Figure 4.18: Hardness vs. austenitization time at different austenitization temperature at the selected tempering temperature 25°C.

Figure 4.19 shows the as quenched hardness of Steel B versus the amount of retained austenite. Initially the hardness increases as the amount of retained austenite increases because the carbon content in the martensite phase also increases. As higher amounts of retained austenite, the as-deep-quenched hardness decreases reflecting the lower hardness of retained austenite. Therefore, the amount of retained austenite should be optimized in a hardening treatment.
Figure 4.19: Hardness vs. the amount of retained austenite

Figure 4.20 compares Steel A and B austenitized at 1114°C for 7.5 seconds for the hardness after tempering. They both reach maximum hardness at about the same precipitation temperature of 275 °C. In the as–hardened state, both steels have similar hardness of about Hv750. However, Steel B has slightly higher hardness in the tempered state. This may be due to the fact that Steel B has a rougher surface finish as observed in Section 4.1.2. The rougher surface finish resulted in more effective heat transfer and more carbide dissolution, and subsequently higher hardness during the hardening treatment. In addition to the surface roughness difference, more reason is given in next section.
4.2.1 Microstructure of hardened steels

The SEM micrographs were taken after the heat treatment at each condition. Figure 4.21 shows a set of SEM images for the hardened Steel B which was austenitized at 1114°C for 6 seconds, 7.5 seconds, 11.25 seconds and 18 seconds respectively, followed by precipitation hardening at 250°C. Image (a) has shorter austenitizing time and appears to have more undissolved carbides in a unit area which indicates less carbide dissolution in comparison to image (b) to (d), while image (d) has longer austenitizing time and appears to have less undissolved carbide. Figure 4.22 shows the SEM images for the hardened steel at various austenitizing temperatures with fixed austenitizing time. The difference is less visible.
Figure 4.21: Microstructure of Steel B austenitized at 1114°C, for 6 seconds, 7.5 seconds, 11.25 seconds and 18 seconds respectively, followed by precipitation hardened at 250°C. (a) austenitizing for 18 seconds, (b) austenitizing for 11.25 seconds, (c) austenitizing for 7.5 seconds and (d) austenitizing for 6 seconds.
Steel B: Austenitizing for 7.5 seconds and tempered at 250°C (8000x)

Figure 4.22: Microstructure of Steel B austenitized at 1081°C 1114°C 1143°C, respectively, for 7.5 seconds and followed by precipitation hardened at 250°C. (a) austenitizing at 1080°C, (b) austenitizing at 1114°C, (c) austenitizing at 1143°C.
4.3 Secondary carbide size distribution

Based on the procedure that is described in Section 3.4, the secondary carbide size distribution was analyzed for the as-received (annealed) condition as well as the deep quenched condition. The data were exported to an EXCEL file for analysis. The secondary carbide characteristics of soft Steel A and B are summarized in Table 4.2. Although the similarity of the two steels, the subtle difference between Steel A and B in terms of carbide size, volume fraction as well as the carbide density (#of particles per 100 $\mu$m$^2$) can be seen. A histogram is plotted as shown in Figures 4.23 for Steels A and B. Steel A seems having more smaller carbides than Steel B.

Table 4.2: Summary of Carbide analysis result.

<table>
<thead>
<tr>
<th></th>
<th>Steel A</th>
<th>Steel B</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total # of particles (5 images)</td>
<td>576</td>
<td>644</td>
</tr>
<tr>
<td>Mean radius ($\mu$m)</td>
<td>0.18894</td>
<td>0.17808</td>
</tr>
<tr>
<td>Max radius ($\mu$m)</td>
<td>0.65436</td>
<td>0.56865</td>
</tr>
<tr>
<td>Min radius ($\mu$m)</td>
<td>0.02506</td>
<td>0.02506</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>0.13131</td>
<td>0.11474</td>
</tr>
<tr>
<td>Variance</td>
<td>0.01724</td>
<td>0.01317</td>
</tr>
<tr>
<td>Area (Volume) fraction (%)</td>
<td>11.89</td>
<td>11.27</td>
</tr>
<tr>
<td>Density (# of carbides/100$\mu$m$^2$)</td>
<td>71.55</td>
<td>80.00</td>
</tr>
<tr>
<td>ROI ($\mu$m$^2$)</td>
<td>161</td>
<td>161</td>
</tr>
</tbody>
</table>
The subtle difference between Steels A and B can be also detected by analyzing the distribution functions before and after hardening. By comparing Figure 4.24 and 4.25, steel B seems dissolving more carbides than Steel A based on the slightly larger gap between the blue and the red curves that represent the carbide size distribution curves for the annealed and hardened states, respectively. This explains that Steels A and B had slightly different hardening behavior as we observed in Figure 4.20. The rougher surface finish of steel B may have played a role in effective heat transfer during austenitization and subsequent higher hardness than steel A.

Table 4.3 lists the carbide analysis numerical results from the selected hardening parameters. Those results can be further plotted to show the carbide size characteristics as function of austenitization temperature and austenitization time.
Figure 4.24: Histogram of the secondary carbide particle distribution for Steel A

Figure 4.25: Histogram of the secondary carbide particle distribution for Steel B
Table 4.3: Summary of carbide particle distribution of Steel B at the selected hardening settings.

<table>
<thead>
<tr>
<th>Austenitization Temperature</th>
<th>Soft steel B</th>
<th>1081(°C)</th>
<th>1114(°C)</th>
<th>1143(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Austenitization time (s)</td>
<td></td>
<td>7.5</td>
<td>6.0</td>
<td>7.5</td>
</tr>
<tr>
<td>Average Radius</td>
<td>0.17808</td>
<td>0.17254</td>
<td>0.18405</td>
<td>0.19870</td>
</tr>
<tr>
<td>Std Dev</td>
<td>0.11474</td>
<td>0.08359</td>
<td>0.08797</td>
<td>0.09696</td>
</tr>
<tr>
<td>Variance</td>
<td>0.01317</td>
<td>0.00699</td>
<td>0.00774</td>
<td>0.00940</td>
</tr>
<tr>
<td>Area/volume fraction</td>
<td>11.27</td>
<td>6.74</td>
<td>8.51</td>
<td>6.67</td>
</tr>
<tr>
<td>Carbide density</td>
<td>80.00</td>
<td>58.39</td>
<td>65.09</td>
<td>43.48</td>
</tr>
<tr>
<td>Retained austenite</td>
<td>15.73</td>
<td>19.41</td>
<td>20.99</td>
<td>25.60</td>
</tr>
<tr>
<td>Hardness Hv</td>
<td>320</td>
<td>728.7</td>
<td>722.0</td>
<td>735.3</td>
</tr>
<tr>
<td>Vol % Dissolved</td>
<td>4.5</td>
<td>2.8</td>
<td>4.6</td>
<td>6.3</td>
</tr>
<tr>
<td># Dissolved</td>
<td>21.6</td>
<td>14.9</td>
<td>36.5</td>
<td>47.2</td>
</tr>
</tbody>
</table>

Note: 1: * indicates nominal temperature setting.

Figure 4.26 shows the carbide area fraction of carbide particles in a polished surface and the carbide density, defined as the number of particles in 100 μm² of polished planar surface, both as a function of austenitizing temperature. The area fraction, which is equivalent to the volume fraction of carbide, decreases moderately with increasing austenitizing temperature from 1081°C to 1114°C, but decreases at higher rate above 1114°C. The carbide density, in the other hand, decreases fast below 1114°C, but stay nearly constant above 1114°C. These observations suggest that small particles dissolves rapidly at low austenitization temperature, while large particles sustain even at higher austenitizing temperature, but with more significant dissolution, while concurrently keeps their numbers nearly constant. Figure 4.27 shows the carbide area fraction and carbide density as function of austenitizing time. Both decreasing rapidly in the initial a few seconds indicates the rapid carbide dissolution controlled mainly by the diffusion of carbon in the austenite. 

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Figure 4.26: Area fraction and carbide density of hardened steel B as a function of austenitization temperature

Figure 4.27: Area fraction and carbide density of hardened steel B as a function of austenitization time (austenitizing at 1114°C)
Figure 4.28 shows the average radius of carbide particles as a function of austenitizing temperature. The initial rapid increase in average radius indicates the dissolution of small particles that becomes increasingly more complete as austenitizing temperature is increased from 1081°C to 1114°C. Above 1114°C, small particles are largely gone by the combined action of dissolution and coarsening, and only large particles remain. The nearly constant values of average radius above 1114°C suggest that the decrease in average radius due to the dissolution is offset by the increase in average radius due to the coarsening.

Figure 4.28: Average carbide radius of hardened steel B as a function of austenitization temperature.

Figure 4.29 shows the average carbide particle radius with increasing austenitizing time at
1114°C. Again, the average carbide particle radius increases rapidly during initial a few seconds, reflecting the disappearance of small particles due to mainly the dissolution. Beyond 7.5 seconds, the average radius remained merely constant at about 0.19 μm as a result of the balance rate of dissolution and coarsening.

Figure 4.29: Average carbide radius of hardened steel B as a function of austenitization time.

Figures 4.30 and 431 show the true retained austenite as a function of mean carbide radius and the amount of carbide dissolved, respectively. The “true retained austenite” refers to the amount of austenite excluding the carbide volume fraction. As discussed in Section 3.1.5, the retained austenite was calculated by measuring amount of martensite. With the carbide image
analysis, the volume fraction of the carbide can be determined and subsequently the “true retained austenite can be determined as well. The true retained austenite increases with increasing of mean carbide radius. The retained austenite decreases with increasing of carbide dissolution initially, but then increases with increasing the amount of carbide dissolution. This is due to the fact that both carbon and chromium are austenite stabilizer. The more carbon and chromium diffuse into the austenite matrix and more austenite will be retained after martensitic transformation during hardening heat treatment.

Figure 4.30: True retained austenite of Steel B as a function of mean carbide radius after austenitization
Figures 4.32 and 4.33 show the deep quenched hardness as a function of the mean carbide radius and the amount of carbide dissolution, respectively. The larger carbide size indicates insufficient carbide dissolution or more coarsening reaction, and it results in lower hardness. However, when more carbide is dissolved, retained austenite will increase. Since retained austenite is a soft phase, therefore hardness decreases after dissolving more than 5% of carbide.
Figure 4.32: Hardness of deep quenched Steel B as a function of mean carbide radius

Figure 4.33: Hardness of Steel B as a function of amount (%) of carbide dissolved after deep quenching
5. Modeling of the dissolution and coarsening of secondary carbide particles

During the heating of an alloy consisting of a matrix phase (solid solution) and second phase particles as in austenitizing a tool steel or a martensitic stainless steel, the second phase particles dissolve into the matrix as the solubility of the second phase increases with increasing temperature. The particle dissolution may also be accompanied by particle coarsening which is driven by the energy of the particle-matrix interface. Thus, the second phase particles in a heat-treated alloy have a size distribution that depends on the kinetics of not only dissolution but also coarsening.

Controlling particle size distribution is a critical issue in the commercial heat treatment of a particle containing alloy as the particle size directly affects to the performance of the heat treated alloy. Particle size is also linked to the amount of particle dissolution into the matrix that determines the mechanical properties of the heat-treated alloy, as in the hardening of hypereutectoid steel. Thus, heating schedule must be optimized to obtain sufficient particle dissolution, i.e., solutionizing, while minimizing particle coarsening. Traditionally, this is achieved by experimentally adjusting the holding temperature and time for optimal microstructure and properties. While such an empirical method has often proven satisfactory in practice, it does have limitations, particularly when applied to a continuous heat-treating process, as the dissolution and coarsening of second phase particles may progress even during the heating of the alloy to the holding temperature.
5.1 Particle size distribution

To address the kinetics of particle dissolution and coarsening during heating and holding in a continuous heat treatment, a simulation model was developed that predicts the final particle size distribution and the amount of particle dissolution.

5.1.1 Particle size distribution

Consider a unit volume of an alloy consisting of a matrix and spherical particles that have a known initial size distribution \( n_0(r) \) of particle radius \( r \) as shown in Figure 5.1. Figure 5.1 schematically shows a typical secondary particle size distribution based on the experimental results described in the section 4.3. The particle size distribution is asymmetric. By taking the natural logarithm, the \( n_0(r) \) becomes \( N_0(x) \), where \( x = \ln r \). \( N(x) \) is a symmetric distribution as shown in the figure 5.2 below. Such a symmetric logarithmic distribution has been widely found to be best applicable to particle size distribution (PSD) in naturally occurring particle containing systems. The best curve fitting of data is normally achieved with a normal or Gaussian distribution, so that for the initial state we may write:

\[
N_0(x) = \frac{1}{\sigma_0 \sqrt{2\pi}} \exp \left[ -\frac{(x - x_0)^2}{2\sigma_0^2} \right]
\]

(5.1)

where \( N_0(x) \) is the probability of finding particles at \( x \) defined as \( x = \ln r \), \( x_0 \) is the initial mean value of \( x \) (initial mode), and \( \sigma_0^2 \) is the initial value of the variance, as shown in Figure 5.2.
**Figure 5.1:** Particle size distribution at time zero

**Figure 5.2:** Log-normal particle size distribution at time zero.
Eq. (5.1) can be rewritten for the actual size distribution at time 0, \( n_0(r) \), as:

\[
n_0(r) = \frac{1}{\sigma_0 \sqrt{2\pi}} \exp\left[-\frac{[(\ln r) - (\ln r_0)]^2}{2\sigma_0^2}\right]
\]

or

\[
n_0(r) = \frac{1}{\sigma_0 \sqrt{2\pi}} \exp\left[-\frac{[(\ln r / r_0)]^2}{2\sigma_0^2}\right]
\]

where \( r_0 \) is the initial value of the mean radius given by \( r_0 = e^x \).

5.1.2 Particle dissolution

Suppose both the particle dissolution and coarsening during heating become significant when the temperature reaches \( T_1 \). Assume also that at a given instantaneous temperature, a single value of dissolution rate (in m/s) applies to all particles regardless of their radius. Then, the size distribution after a time increment \( \Delta t_1 \) at \( T_1 \) is obtained by the translation of \( n_0(r) \) to \( n(r') = n_0(r + \Delta r_{11}) \) where \( \Delta r_{11} \) is the decrease in particle radius due to the dissolution over \( \Delta t_1 \), which applies to all the particles, as shown in Figure 5.3 and 5.4. Since the translational shift does not alter the variance \( \sigma_0^2 \), the new particle size distribution at time \( \Delta t_1 \), \( n_{11}(r) \), is given by:

\[
n_{11}(r) = n_0(r') = \frac{1}{\sigma_0 \sqrt{2\pi}} \exp\left[-\frac{[(\ln r') - (\ln r_0)]^2}{2\sigma_0^2}\right]
\]
\[ n_{i_1}(r) = \frac{1}{\sigma_0 \sqrt{2\pi}} \exp \left\{ -\frac{[\ln(r + \Delta r_{i_1}) - \ln r_0]^2}{2\sigma_0^2} \right\} \]

\[ = \frac{1}{\sigma_0 \sqrt{2\pi}} \exp \left\{ -\frac{[\ln r(1 + \Delta x_{i_1}) - \ln r_0]^2}{2\sigma_0^2} \right\} \]

\[ = \frac{1}{\sigma_0 \sqrt{2\pi}} \exp \left\{ -\frac{[x_0 + \ln(1 + \Delta x_{i_1})]^2}{2\sigma_0^2} \right\} \]

\[ = \frac{1}{\sigma_0 \sqrt{2\pi}} \exp \left\{ -\frac{[x_0 - \ln(1 + \Delta x_{i_1})]^2}{2\sigma_0^2} \right\} \]

\[ = \frac{1}{\sigma_0 \sqrt{2\pi}} \exp \left\{ -\frac{(x_{i_1} - x_0)^2}{2\sigma_0^2} \right\} = N_{i_1}(x) \]  

(5.4)

where \( x_{i_1} = \ln r_{i_1} = x_0 - \ln (1 + \Delta x_{i_1}) \).
Figure 5.3: Translational shift of particle size distribution from blade line to red line due to dissolution over $\Delta t_1$.

Figure 5.4: Log-normal particle size distribution at time zero (in black) shifting to red line after incremental time $\Delta t_1$. 
Thus, the mean particle radius after $\Delta t_1$ in the absence of coarsening, $r_{11}$, is calculated from:

$$r_{11} = e^{x_{11}}$$  \hspace{1cm} (5.5)$$

and the decrease in mean radius, $\Delta r_{11}$, is given by:

$$\Delta r_{11} = r_0 - r_{11} = e^{x_0} - e^{x_{11}}$$

$$= e^{x_0} - e^{x_0 \ln (1 + \Delta x_{11})}$$

$$\Delta r_{11} = e^{x_0} [1 - e^{-\ln (1 + \Delta x_{11})}]$$  \hspace{1cm} (5.6)$$

5.1.3 Particle coarsening

Over the same time increment $\Delta t_1$, the particles may also coarsen by Ostwald ripening. Let $r_{12}$ be the mean particle radius after the dissolution and coarsening over $\Delta t_1$ as shown in Figure 5.5 and 5.6, so that:

$$x_{12} = \ln r_{12} = x_0 - \ln (1 + \Delta x_{11}) + \Delta x_{12}$$  \hspace{1cm} (5.7)$$

where $\Delta x_{12}$ is the shift of the mode of $N(x)$ due to particle coarsening. It is denoted that “1” at the second digit of the subscript as the dissolution and “2” at the second digit of the subscript as the coarsening, while the first digit of the subscript is sequential step. For example, $r_{31}$ is the particle radius at the third step of dissolution and $r_{32}$, is the radius at the third step of the coarsening. Then,
the new log-normal distribution is given by:

\[
N_{12}(x) = \frac{1}{\sigma_1 \sqrt{2\pi}} \exp \left\{ -\frac{\left(x - [x_0 - \ln(1 + \Delta x_{11}) + \Delta x_{12}]\right)^2}{2\sigma_0^2} \right\}
\]

\[
= \frac{1}{\sigma_1 \sqrt{2\pi}} \exp \left[ -\frac{(x - x_{12})^2}{2\sigma_1^2} \right]
\]

(5.8)

where \(x_{12} = x_0 - \ln(1 + \Delta x_{11}) + \Delta x_{12}\) and the variance also has a new value \(\sigma_1^2\).

Figure 5.5 Translational shift of particle size distribution from solid red line to dashed red line due to coarsening over \(\Delta t_1\).
Figure 5.6  Log-normal translational shift of particle size distribution from solid red line to dashed red line due to coarsening over $\Delta t_1$

Since particle coarsening should not affect the total volume of particles,

$$V_{11} = V_{12}$$

(5.9)

where $V_{11}$ is the total volume of the particles at $t = \Delta t_1$ in the absence of particle coarsening, and $V_{12}$ is that which accounts for particle coarsening. $V_{11}$ and $V_{12}$ are given respectively, by:

$$V_{11} = \int_{-\infty}^{\infty} \frac{4\pi}{3} r^3 \cdot n_{11} (r) \cdot dr = \int_{-\infty}^{\infty} \frac{4\pi}{3} e^{4x} \cdot N_{11} (x) \cdot dx$$

(5.10)

$$V_{12} = \int_{-\infty}^{\infty} \frac{4\pi}{3} r^3 \cdot n_{12} (r) \cdot dr = \int_{-\infty}^{\infty} \frac{4\pi}{3} e^{4x} \cdot N_{12} (x) \cdot dx$$

(5.11)
where \( dr = rdx \) and \( r = e^x \) are used. Substituting Eq. (5-10) in Eq. (5-16) gives

\[
V_{11} = \frac{4\pi}{3} \cdot \frac{1}{\sigma_0 \sqrt{2\pi}} \cdot r \cdot e^{-\frac{(x - x_0 - \ln(1 + \Delta x_{11}))^2}{2\sigma_0^2}} \cdot dr
\]

\[
= \frac{2\sqrt{2\pi}}{3\sigma_0} \int_{-\infty}^{+\infty} r^3 \cdot e^{-\frac{(x - x_0 - \ln(1 + \Delta x_{11}))^2}{2\sigma_0^2}} \cdot dr
\]

\[
= \frac{2\sqrt{2\pi}}{3\sigma_0} \int_{-\infty}^{+\infty} e^{4x} \cdot e^{-\frac{(x - x_0 - \ln(1 + \Delta x_{11}))^2}{2\sigma_0^2}} \cdot dx
\]

\[
= \frac{2\sqrt{2\pi}}{3\sigma_0} \int_{-\infty}^{+\infty} \exp\left\{ -\frac{(x - x_0 - \ln(1 + \Delta x_{11}))^2}{2\sigma_0^2} + 4x \right\} \cdot dx
\]

\[
= \frac{2\sqrt{2\pi}}{3\sigma_0} \int_{-\infty}^{+\infty} \exp\left\{ -\frac{x^2 - 2x\{x_0 - \ln(1 + \Delta x_{11}) + 4\sigma_0^2\} + [x_0 - \ln(1 + \Delta x_{11})]^2}{2\sigma_0^2} \right\} \cdot dx
\]

(5.12)

Eq. (5.12) can be integrated using the formula

\[
\int_{-\infty}^{+\infty} e^{-ax^2 + bx + c} dx = \sqrt{\frac{\pi}{a}} e^{\frac{b^2 - 4ac}{4a}}
\]

(5.13)
where

\[ a = \frac{1}{2\sigma_0^2} \]

\[ b = -2\frac{[x_0 - \ln(1 + \Delta x_{11})] + 4\sigma_0^2}{\sigma_0^2} \]

\[ c = \frac{[x_0 - \ln(1 + \Delta x_{11})]^2}{2\sigma_0^2} \]

\[ b^2 = 4\left[ \frac{x_0 - \ln(1 + \Delta x_{11})}{4\sigma_0^4} \right]^2 + 16\sigma_0^4 + 8\sigma_0^2 [x_0 - \ln(1 + \Delta x_{11})] \]

\[ 4ac = 4\left[ \frac{x_0 - \ln(1 + \Delta x_{11})}{4\sigma_0^4} \right]^2 \]

\[ b^2 - 4ac = 4\left[ \frac{16\sigma_0^4 + 8\sigma_0^2 [x_0 - \ln(1 + \Delta x_{11})]}{4\sigma_0^4} \right] \]

\[ = \frac{16\sigma_0^2 + 8[x_0 - \ln(1 + \Delta x_{11})]}{\sigma_0^2} \]

so that

\[ \frac{b^2 - 4ac}{4a} = \frac{16\sigma_0^2 + 8[x_0 - \ln(1 + \Delta x_{11})]}{4\sigma_0^2} = 8\sigma_0^2 + 4[x_0 - \ln(1 + \Delta x_{11})] \]
The final integral form of Eq. (5.12) is:

\[
V_{11} = \frac{4\pi}{3} \cdot \exp \left[ 8\sigma_0^2 + 4\left(x_0 - \ln(1 + \Delta x_{11})\right) \right]
\]

\[
= \frac{4\pi}{3} \cdot \exp \left[ 4\sigma_0^2 + x_{11} \right] \tag{5.14}
\]

Likewise, substitution of Eq. (5.8) in Eq. (5.11) gives:

\[
V_{12} = \int_{-\infty}^{+\infty} \frac{4\pi}{3} r^3 \cdot n_{12}(r) \cdot dr = \int_{-\infty}^{+\infty} \frac{4\pi}{3} e^{4x} \cdot N_{12}(x) \cdot dx
\]

\[
= \frac{4\pi}{3} \cdot \frac{1}{\sigma_1 \sqrt{2\pi}} \cdot \exp \left\{ -\frac{\left(x - \ln(1 + \Delta x_{11}) + \Delta x_{12}\right)^2}{2\sigma_0^2} \right\} \cdot dx
\]

\[
= 2\sqrt{\frac{2\pi}{3\sigma_1}} \cdot \int_{-\infty}^{+\infty} e^{4x} \cdot \exp \left\{ -\frac{\left(x - \ln(1 + \Delta x_{11}) + \Delta x_{12}\right)^2}{2\sigma_0^2} \right\} \cdot dx
\]

\[
= \frac{4\pi}{3} \cdot \exp \left[ 8\sigma_1^2 + 4\left(x_0 - \ln(1 + \Delta x_{11}) + \Delta x_{12}\right) \right]
\]

\[
= \frac{4\pi}{3} \cdot \exp \left[ 4\sigma_1^2 + x_{12} \right] \tag{5.15}
\]
In general,

\[ V_{n_1} = \frac{4\pi}{3} \exp \left[ 4 \left( 2\sigma_{n-1}^2 + x_{n_1} \right) \right] \]  

(5.16a)

\[ V_{n_2} = \frac{4\pi}{3} \exp \left[ 4 \left( 2\sigma_0^2 + x_{n_2} \right) \right] \]  

(5.16b)

Substituting Eq. (5.14) and (5.15) in Eq. (5.9),

\[ \frac{4\pi}{3} \cdot \exp \left[ 4 \left( 2\sigma_0^2 + x_{i_1} \right) \right] = \frac{4\pi}{3} \exp \left[ 4 \left( 2\sigma_1^2 + x_{i_2} \right) \right] \]

yields:

\[ \sigma_1 = \sqrt{\sigma_0^2 - \frac{\Delta x_{i_2}}{2}} \]  

(5.17)

where \( \Delta x_{i_2} = x_{i_1} - x_{i_2} = \ln r_{i_1} - \ln r_{i_2} \)

The next time increment \( \Delta t_2 \), increases the temperature of the alloy to \( T_1 + \Delta T \). The particle size distribution at the start of the time increment, \( n_{20}(r) \), is given by

\[ n_{20}(r) = n_{i_2}(r) = \frac{1}{\sigma_1 \sqrt{2\pi}} \exp \left\{ -\frac{\left[ \ln (r/r_{i_2}) \right]^2}{2\sigma_1^2} \right\} \]  

(5.18)
where $r_{12}$ is the mean radius at the end of the previous time increment given by Eq. (5.8). Figure 5.7 shows the schematic shift of the particle size distribution from the dashed red line to the solid blue line due to the dissolution over $\Delta t_2$.

Since particle dissolution merely translates the radius distribution uniformly to the left by $\Delta r_{21}$, there is no change in variance $\sigma^2_1$ and, the distribution at the end of $\Delta t_2$ in the absence of coarsening, $n_{21}(r)$, is given by:

$$n_{21}(r) = n_{12}(r + \Delta r_{21}) = \frac{1}{\sigma_1 \sqrt{2\pi}} \exp \left\{ - \frac{[\ln(r + \Delta r_{21})/r_{12}]^2}{2\sigma^2_1} \right\}$$

$$= \frac{1}{\sigma_1 \sqrt{2\pi}} \exp \left\{ - \frac{[\ln r(1 + \Delta x_{21}) - x_{12}]^2}{2\sigma^2_1} \right\}$$

(5.19)
Thus, the corresponding log-normal distribution is

\[
N_{21}(x) = \frac{1}{\sigma_1 \sqrt{2\pi}} \exp\left(-\frac{(x-x_{01} - \ln(1+\Delta x_{11}) - \ln(1+\Delta x_{21}) + \Delta x_{12})^2}{2\sigma_1^2}\right)
\]

\[
= \frac{1}{\sigma_1 \sqrt{2\pi}} \exp\left(-\frac{(x-x_{21})^2}{2\sigma_1^2}\right)
\]

(5.20)

where \( x_{21} = x_0 - \ln(1+\Delta x_{11}) - \ln(1+\Delta x_{21}) + \Delta x_{12} \)

Over the same time increment, particles coarsen to increase the mean radius to a new value \( r_{22} \) so that the \( N(x) \) changes to:

\[
N_{22}(x) = \frac{1}{\sigma_2 \sqrt{2\pi}} \exp\left(-\frac{(x-x_{22})^2}{2\sigma_2^2}\right)
\]

(5.21)

where \( x_{22} = x_0 - \ln(1+\Delta x_{11}) - \ln(1+\Delta x_{21}) + \Delta x_{12} = \Delta x_{22} \) and the variance has a new value \( \sigma_2^2 \).

Figure 5.8 shows the schematic shift of the particle size distribution from the solid blue line to the dashed blue line due to the coarsening over \( \Delta t_2 \).
As coarsening does not alter the total volume of particles $V_{21} = V_{22}$, so that:

$$
\int_0^\infty \frac{4\pi r^3}{3} \cdot n_{21}(r)dr = \int_0^\infty \frac{4\pi r^3}{3} \cdot n_{22}(r)dr
$$

(5.22)

or

$$
\int_{-\infty}^{\infty} \frac{4\pi}{3} e^{4x} \cdot N_{21}(x)dx = \int_{-\infty}^{\infty} \frac{4\pi}{3} e^{4x} \cdot N_{22}(x)dx
$$

(5.23)

Applying the same integration procedure as that of Eq. (5.22) and (5.23), we obtain:
\[ \sigma_2 = \sqrt{\frac{\sigma_1^2 - \Delta x_{22}}{2}} = \sqrt{\frac{\sigma_0^2 - \Delta x_{12} - \Delta x_{22}}{2}} \]  

(5.24)

Likewise, for the \( n \)th time increment,

\[ N_{n1}(x) = \frac{1}{\sigma_{n-1} \sqrt{2\pi}} \exp \left[ -\frac{(x - x_{n1})^2}{2\sigma_{n-1}^2} \right] \]  

(5.25)

\[ N_{n2}(x) = \frac{1}{\sigma_n \sqrt{2\pi}} \exp \left[ -\frac{(x - x_{n2})^2}{2\sigma_n^2} \right] \]  

(5.26)

where

\[ x_{n1} = x_0 - \sum_{i=1}^{n} \ln(1+\Delta x_i) + \sum_{i=1}^{n} \Delta x_{(i-1)2} \]  

(5.27)

\[ x_{n2} = x_0 - \sum_{i=1}^{n} \ln(1+\Delta x_i) + \sum_{i=1}^{n} \Delta x_{i2} \]  

(5.28)

where \( \Delta x_0 = 0 \).

From \( V_{n1} = V_{n2} \),

\[ \int_{-\infty}^{\infty} \frac{4\pi}{3} e^{4x} \cdot N_{n1}(x) dx = \int_{-\infty}^{\infty} \frac{4\pi}{3} e^{4x} \cdot N_{n2}(x) dx \]  

(5.29)
which yields:

$$\sigma_n = \sqrt{\sigma_o^2 - \frac{1}{2} \sum_{i=1}^{n} \Delta x_{i/2}}$$  \hspace{1cm} (5.30)

The absence of $\Delta x_{i}$ in Eq. (5.30) is consistent with the effects of dissolution which does not alter the variance.

Finally, from $x_{n2} = x_{02} - \sum_{i=1}^{n} \ln(1 + \Delta x_{i}) + \sum_{i=1}^{n} \Delta x_{i/2}$ the mean diameter $\bar{r}$ after the $n$th time increment is calculated from:

$$\bar{r} = e^{x_{n2}} = \exp\left[x_{02} - \sum_{i=1}^{n} \ln(1 + \Delta x_{i}) + \sum_{i=1}^{n} \Delta x_{i/2}\right]$$  \hspace{1cm} (5.31)

5.1.4 Numerical simulation

The above model, represented by Eqs. (5.26), (5.28) and (5.30), permits numerical simulation of the dissolution and coarsening of particles in a heat treatment under any heating schedule. Consider a case where the alloy is heated gradually from the initial temperature $T_o$ to the holding temperature $T_h$ under the schedule:

Heating stage: \hspace{1cm} $T(t)$ \hspace{1cm} ($T_o \leq T < T_h$)

Holding stage: \hspace{1cm} $T_h$

where $T(t)$ is an increasing function of time $t$. Assume that the specimen has a small dimension so that the specimen temperature is uniform at all times. Assume also that particle dissolution and
coarsening are both insignificant until temperature reaches $T_i$, at which the particles have the initial size distribution given by Eq. (5.1).

To simulate the particle size distribution at progressive computation steps, either temperature or time may be incremented. In the following procedure, we increment the temperature. Thus, in each step of computation, temperature increases from $T_i$ to $T_i + \Delta T$ over a time increment of $\Delta t_i$ calculated from $\Delta t_i = \Delta T/\dot{T}_i$ where $\dot{T}_i$ is the instantaneous heating rate at $T_i$.

The critical terms in Eqs. (5.26), (5.28) and (5.30) that need to be calculated are $\Delta x_{i1}$ and $\Delta x_{i2}$ which represent the changes in $\ln r$ due, respectively, to the dissolution and coarsening in the $i$th step. To illustrate the computation procedure, consider the first step where the temperature is $T_i$. The change in $\ln r$ due to dissolution, $\Delta x_{i1}$, is calculated with:

$$
\Delta x_{i1} = x_{i1} - x_{o2} = \ln(r_{i1} / r_{o2}) = \ln\left(\frac{r_{o2}}{r_{i1}} - \Delta r_{i1}\right) / r_{o2} = \ln\left(\frac{r_{o2}}{r_{i1}} - \nu_D(T_1)\Delta t_1\right) / r_{o2}
$$

(5.32)

where $\nu_D(T_1)$ is the rate of dissolution in m/s at $T_1$ and $\Delta t_1$ is the time of Step 1. The value of $\nu_D(T_1)$ is calculated from the diffusion-controlled kinetics of dissolution (See Section 5.2). The change in $\ln r$ due to coarsening, $\Delta x_{i2}$, is calculated with:

$$
\Delta x_{i2} = x_{i2} - x_{i1} = \ln\left(\frac{r_{i2}}{r_{i1}} / \frac{r_{i1}}{r_{i1}}\right) = \ln\left(\frac{r_{i1}}{r_{i2}} + \Delta r_{i2}\right) / r_{i1} = \ln\left(\frac{r_{i1}}{r_{i2}} + v_C^{m}(T_1)\Delta t_1\right) / r_{i1}
$$

(5.33)

where $v_C^{m}(T_1)$ is the rate of coarsening in m/s at $T_1$. The value of $v_C^{m}(T_1)$ is calculated from Ostwald ripening kinetics (See Section 5.2). The value of $r_{i1}$ already calculated in Eq. (5.32) applies to Eq. (5.33).
The temperature is then increased for the next step to $T_2 = T_1 + \Delta T$ and the above procedure is repeated to calculate $\Delta x_{21}$ and $\Delta x_{22}$. Performing the same for further steps leads to the computation of $\Delta x_{n1}$ and $\Delta x_{n2}$ with:

$$\Delta x_{n1} = x_{n1} - x_{(n-1)2} = \ln(r_{n1} / r_{(n-1)2}) = \ln\left[(r_{(n-1)2} - \Delta r_{n1})/r_{(n-1)2}\right] = \ln\left[(r_{(n-1)2} - v_C(T_n)\Delta T_n)/r_{(n-1)2}\right]$$

$$\Delta x_{n2} = x_{n2} - x_{n1} = \ln(r_{n2} / r_{n1}) = \ln\left[(r_{n1} + \Delta r_{n2})/r_{n1}\right] = \ln\left[r_{n1} + v_C^m(T_n)\Delta T_n\right]/r_{n1}$$

The values of $\Delta x_{n1}$ and $\Delta x_{n2}$, calculated up to $n$, are then used in Eqs. (5.28) and (5.30) to calculate the mean value of $x_{n2}$ and the standard deviation $\sigma_n$.

$$x_{n2} = x_{02} - \sum_{i=1}^{n} \ln(1 + \Delta x_{i1}) + \sum_{i=1}^{n} \Delta x_{i2}$$

$$\sigma_n = \sqrt{\sigma_o^2 - \frac{1}{2} \sum_{i=1}^{n} \Delta x_{i2}}$$

Once the value of $x_{n2}$ is calculated, the mean particle diameter is calculated with Eq. (5.31)

$$\bar{r} = e^{x_{n2}} = \exp\left[x_{02} - \sum_{i=1}^{n} \ln(1 + \Delta x_{i1}) + \sum_{i=1}^{n} \Delta x_{i2}\right]$$

5.1.5 Heating and holding stages

The above procedure obviously applies to both the heating and holding stages of a heat treatment. In the heating stage, $\Delta T > 0$ (at a fixed value), whereas in the holding stage, $\Delta T = 0$. 

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The transition from the heating to holding stages occurs when $T_n$ reaches $T_h$.

### 5.1.6 Total amount of dissolution

The cumulative volume of particle dissolution $\Delta V_n$ is critical information required in a solution heat treatment in general. The model permits calculating it simply from $\Delta V_n = V_{n_2} - V_{n_2}$ where $V_{n_2}$ and $V_{n_2}$ are, respectively, the initial and final values of the total volume of particles. As shown in Eqs. (5.10) - (5.14), $V_{n_2}$ and $V_{n_2}$ are calculated as shown below:

$$V_0 = \frac{4\pi}{3} \int_0^\infty r^3 n_0(r)dr$$

$$= \frac{4\pi}{3} \int_{-\infty}^\infty e^{4x} N_0(x)dx$$

$$= \frac{2\sqrt{2\pi}}{3\sigma_0} \int_{-\infty}^\infty e^{4x} \exp \left[ -\frac{(x-x_0)^2}{2\sigma_0^2} \right] dx$$

$$= \frac{4\pi}{3} \exp \left[ 4(2\sigma_0^2 + x_0) \right]$$

(5.36)

Likewise,

$$V_{n_2} = \frac{4\pi}{3} \int_0^\infty r^3 n_{n_2}(r)dr$$

$$= \frac{2\sqrt{2\pi}}{3\sigma_n} \int_{-\infty}^\infty e^{4x} \exp \left[ -\frac{(x-x_{n_2})^2}{2\sigma_n^2} \right] dx$$
\[ \frac{4\pi}{3} \exp \left[ 4\left(2\sigma_n^2 + x_n^2\right) \right] \]  

(5.37)

Thus,

\[ \Delta V_n = \frac{4\pi}{3} \left\{ \exp \left[ 4\left(2\sigma_0^2 + x_0\right) \right] - \exp \left[ 4\left(2\sigma_n^2 + x_n^2\right) \right] \right\} \]  

(5.38)

Then the number of moles of the second phase that dissolved into the matrix, \( N_p \), is

\[ N_p = \frac{\Delta V_n}{V_p} \]

where \( V_p \) is the molar volume of the particles. Thus, the number of moles of an element A in the second phase \( \text{A}_a\text{B}_b\text{C}_c\ldots\ldots\text{N}_n \) gained in the matrix is \( a \cdot N_p \), and the mass of element A gained in the matrix \( M_A \) is

\[ M_A = a \cdot N_p \mu_A \]

where \( \mu_A \) is the molar mass of A.
5.2 Rate equations for particle dissolution and coarsening

To predict the change in particle distribution during heating to and holding at the solutionizing (austenitizing) temperature, the rates of particle dissolution and coarsening (Ostwald ripening) need to be addressed. Expressions are developed for the rates of particle dissolution and coarsening that can be accommodated in the particle size distribution simulation model described in Section 5.1.

5.2.1 Rate of particle dissolution

We first develop a mathematical expression for the rate (velocity) of the interface of a particle undergoing dissolution in the absence of coarsening. To obtain a simple expression of the dissolution rate, the following assumptions are made:

a) The dissolution rate is controlled by the diffusion of the solute, Cr in this case, in the matrix (austenite).

b) The dissolving particles are assumed to be spherical.

c) The concentration profile of the solute in the matrix at the interface of a particle of radius r at any temperature during heating or holding is the same as the one that would be obtained by allowing the particle to dissolve isothermally to the radius (r).

d) For simplicity, we adopt Zener’s linear approximation for the concentration profile which is defined by the tie-line concentration of the austenite and $v_D$ the far-field concentration and the global mass balance.

e) No impingement of diffusion zones of adjacent particles is considered. (A long-time treatment could account for diffusion-zone impingement).
Suppose a (carbide) particle whose initial radius was $r_0$ has a radius $r$ as a result of dissolution during heating from some initial temperature $T_i$ to $T$. As a result, the rejected solute is piled up at the interface, which produces a concentration gradient driving the diffusion of the solute away from the interface. The solute concentration profile is depicted schematically in Figure 5.9.

![Figure 5.9: Solute concentration profile across particle-matrix](image)

The mass balance at the interface is given by:

$$4\pi r^2 \left( C^K_{Cr} - C^\infty_{Cr} \right) dr = -4\pi r^2 \left[ D \left( \frac{\partial C}{\partial R} \right) \right] dt$$

or
\[
\frac{dr}{dt} = -\frac{D}{\left(C_{Cr}^e - C_{Cr}^r\right)} \left(\frac{\partial C}{\partial r}\right)_{r}
\]

(5.39)

where \(r\) is the distance from the center of the particle, \(D\) is the diffusivity of the solute in the austenite, and \(C_k\) is the tie-line solute concentration in the particle. Zener’s linear approximation gives the global mass balance:

\[
\frac{1}{2} L(C_{Cr}^r - C_{Cr}^0) = (r_0 - r) \cdot (C_{Cr}^0 - C_{Cr}^r)
\]

which gives the concentration gradient as:

\[
\left(\frac{\partial C}{\partial R}\right)_{r} = \frac{(C_{Cr}^r - C_{Cr}^{\infty})^2}{2 \cdot (C_{Cr}^k - C_{Cr}^{\infty})(r - r_0)}
\]

(5.40)

Substituting Eq. (2) in Eq. (1), we obtain:

\[
\frac{dr}{dt} = -\frac{D}{\left(C_{Cr}^k - C_{Cr}^r\right)} \left(\frac{\partial C}{\partial r}\right)_{r} = v_D = -\frac{D}{2 \cdot (C_{Cr}^k - C_{Cr}^{\infty})} \cdot \frac{(C_{Cr}^r - C_{Cr}^{\infty})^2}{(C_{Cr}^k - C_{Cr}^{\infty})(r - r_0)}
\]

(5.41)

Thus,

\[
\int_{r_0}^{r} (r_0 - r) \cdot dr = \int_{0}^{t} \frac{D}{2 \cdot (C_{Cr}^k - C_{Cr}^r)} \cdot \frac{(C_{Cr}^r - C_{Cr}^{\infty})^2}{(C_{Cr}^k - C_{Cr}^{\infty})} \cdot dt
\]

(5.42)

which upon integration gives
\[(r_0 - r)^2[r_0^2 = \frac{D}{(C_{Cr}^K - C_{Cr}^\alpha)} \cdot \left(\frac{(C_{Cr}^\alpha - C_{Cr}^\infty)^2}{(C_{Cr}^K - C_{Cr}^\infty) \cdot (C_{Cr}^K - C_{Cr}^\infty)} \cdot t\right)]_0 \quad (5.43)\]

or

\[r = r_0 - \sqrt{\alpha \cdot D \cdot t} \quad (5.44)\]

where is \(\alpha\) rate constant defined as:

\[\alpha = \frac{(C_{Cr}^\alpha - C_{Cr}^\infty)^2}{(C_{Cr}^K - C_{Cr}^\infty) \cdot (C_{Cr}^K - C_{Cr}^\infty)}\]

and \(t\) is the time that would be needed for the particle radius to decrease from its initial value \(r_0\) to \(r\) if held isothermally at a temperature \(T\).

Differentiating Eq. (5.44), we obtain:

\[v_D = \frac{1}{2} \sqrt{\frac{\alpha \cdot D}{t}} \quad (5.45)\]

Consider a time increment \(\Delta t_i\) over which the radius decreases from its initial value \(r_0\) to \(r_{i1}\) at \(T_i\). From Eqs. (5.43) and (5.45),

\[r_{i1} = r_0 - \Delta r_{i1} = r_0 - \sqrt{\alpha_{i1}D_{i1}\Delta t_i} \quad (5.46)\]

\[\Delta r_{i1} = v_{D_i}\Delta t_i = \frac{\Delta t_i}{2} \sqrt{\frac{\alpha_{i1}D_{i1}}{\Delta t_i}} \quad (5.47)\]
where $\Delta r_{11}$ is the decrease in $r$ over $\Delta t_1$. In the next time increment $\Delta t_2$, temperature increases by $\Delta T$ to $T_2$ and Eqs. (5.43) and (5.45) give:

$$r_{21} = r_{11} - \Delta r_{11} = r_0 - \sqrt{\alpha_2 D_2 t_2}$$

(5.48)

$$\Delta r_{21} = v_d \Delta t_2 = \frac{\Delta t_2}{2} \sqrt{\frac{\alpha_2 D_2}{t_2}}$$

(5.49)

where $\Delta r_{21}$ is the decrease in $r$ over $\Delta t_2$, $t_2$ is the time that would be needed for the particle radius to decrease from its initial value $r_0$ to $r_{21}$ if held isothermally at a temperature $T_2$, $\alpha_2$ and $D_2$ are, respectively the rate constant and the diffusivity at $T_2$.

Combining the equation (5.48) and (5.49), we obtain:

$$\frac{\Delta t_2}{2} \sqrt{\frac{\alpha_2 D_2}{t_2}} = r_{11} - r_0 + \sqrt{\alpha_2 D_2 t_2}$$

(5.50)

which is a quadratic equation of $\sqrt{t_2}$. Taking the positive root, we have:

$$\sqrt{t_2} = \frac{r_0 - r_{11} + \sqrt{(r_{11} - r_0)^2 + 2\alpha_2 D_2 \Delta t_2}}{2\sqrt{\alpha_2 D_2}}$$

(5.51)

Thus, substituting Eq. (5.51) in Eqs. (5.48) and (5.49) yields:
In the $n$th time increment $\Delta t_n$, temperature increases by $\Delta T$ to $T_n$, and Eqs. (5.43) and (5.45) give:

$$r_{n1} = r_{(n-1)1} - \Delta r_{n1} = r_0 - \sqrt{\alpha_n D_n t_n}$$

(5.54)

$$\Delta r_{n1} = v_{Dn} \Delta t_n = \frac{\Delta t_n}{2} \sqrt{\frac{\alpha_n D_n}{t_n}}$$

(5.55)

Thus,

$$r_{n1} = r_0 - \frac{r_{(n-1)1} + \sqrt{(r_{(n-1)1} - r_0)^2 + 2 \alpha_n D_n \Delta t_n}}{2}$$

(5.56)

$$\Delta r_{n1} = v_{Dn} \Delta t_n = \frac{\alpha_n D_n \Delta t_n}{r_0 - r_{(n-1)1} + \sqrt{(r_{(n-1)1} - r_0)^2 + 2 \alpha_n D_n \Delta t_n}}$$

(5.57)

Eqs. (5.56) and (5.57) directly applies to the particle dissolution model.
5.2.2 Rate of particle coarsening:

It is well established that the mean radius and the rate of coarsening of sphere particles undergoing Ostwald ripening due to volume diffusion are given by:\(^43\):

\[
\bar{r}^3 - \bar{r}_0^3 = \frac{CDC^\infty C_m \gamma}{RT} t
\]

(5.58)

\[
\frac{d\bar{r}}{dt} = V \frac{C CDC C_m \gamma}{3RT} \frac{1}{\bar{r}^3}
\]

(5.59)

Where coefficient C is \(8/9\) which was proposed by LSW\(^35,36\), \(D\) is the diffusivity of the solute, \(C^\infty\) is the equilibrium solubility of the solute in the matrix phase (austenite), \(V_m\) is the molar volume of the particle material, \(R\) is the gas constant, and \(\gamma\) is the energy of the particle-matrix interface.

Over the initial time increment \(\Delta t_1\) at \(T_1\), the radius increases from \(r_1\) to \(r_2\). From Eq. (5.59),

\[
\Delta r_2 = r_2 - r_1 = \frac{CD_1 C^\infty C_m \gamma}{3RT_1} \frac{1}{r_1^2} \Delta t_1 = \frac{CD_1 C^\infty C_m \gamma}{3RT_1} \frac{1}{r_{11}^2} \Delta t_1
\]

(5.60)

where \(r_{11} = r_0 - \Delta r_{11}\).

Likewise,

\[
\Delta r_{n2} = r_{n2} - r_{(n-1)1} = \frac{CD_n C^\infty C_m \gamma}{3RT_n} \frac{1}{r_{n1}^2} \Delta t_{n-1}
\]

(5.61)

where \(r_{n1} = r_{(n-1)2} - \Delta r_{n1}\). The values of \(\Delta r_{n1}\) are calculated with Eq. (5.57).
6. Simulation verification and discussion

Based on the material characterization results, Steels A and B appeared to be very much similar in general in terms of secondary carbide characteristics as they are well spheroidized and uniformly distributed in the ferrite matrixes for both Steels A and B. The carbide dissolution and coarsening model verification was then focused on Steel B. For the modeling verification, five austenitization data points were selected as listed in Table 6.1. The goal is to verify the model using the experimental results from the annealed state and the hardened state for various hardening treatment conditions. The ultimate goal is to predict the mechanical properties of the hardened materials.

Table 6.1: Selected data points for modeling verification

<table>
<thead>
<tr>
<th>Nominal austenitization time</th>
<th>Nominal austenitization temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1081°C</td>
</tr>
<tr>
<td>6 s</td>
<td></td>
</tr>
<tr>
<td>7.5 s</td>
<td>X</td>
</tr>
<tr>
<td>18 s</td>
<td></td>
</tr>
</tbody>
</table>

In order to carry out numerical calculations for verifying the model that was developed in the previous chapter, a few resources for the data have to be obtained. They are the thermodynamic data of the alloy, the kinetic data of the diffusion-controlled carbide dissolution and coarsening, and the temperature profiles of the austenitization furnace.
6.1 Thermodynamic data

The simulation is based on the assumption of local equilibrium at the carbide and austenite moving interface. This means that the compositions of the ferrite, the austenite and the carbide at the phase interface correspond to the local equilibrium values. The concentrations can thus be evaluated from thermodynamic information. In this study, the chromium concentrations in the austenite and the carbide phases were obtained using ThermoCalc\textsuperscript{®}. Isothermal sections of the Fe-Cr-C phase diagram were obtained with the assumption that the local equilibrium state was reached at the interface. Figures 6.1 and 6.2 show examples of the Fe-rich corner of the isothermal sections at 1173 K (900°C). The composition of the alloy falls into the two-phase austenite (γ-Fe) and secondary carbide (M\textsubscript{23}C\textsubscript{6}) region. In the temperature range of austenitization, M\textsubscript{23}C\textsubscript{6} is the stable carbide phase. The boundary condition at the moving interface between γ-Fe and M\textsubscript{23}C\textsubscript{6}, defined by the operating tie-line, has to satisfy the condition that, for every diffusing species, the interface velocity obtained from the mass balance is the same. Using the tie-line rule, the chromium concentration in the phases of ferrite, austenite and carbide at each temperature can be determined, as listed in the Table 6.3.

By plotting the chromium concentration in each phase, carbide or austenite, against the temperature and applying a best fitting curve, chromium concentration $C_{\gamma}^{Cr}$ and $C_{\delta}^{K}$ can be expressed as a function of temperature as given by Eqs (6.1) and (6.2). These functions are used in the numerical calculations.

\[
C_{\gamma}^{Cr} = 7 \cdot 10^{-6} T^2 - 0.003 \cdot T + 1.9867 \quad (6.1)
\]
\[ C_{Cr}^K = 4 \cdot 10^{-5} T^2 - 0.1344 + 178.56 \cdot T + 1.9867 \] (6.2)

Figure 6.1: The Fe-rich corner of the isothermal section at T=1173°C.

Figure 6.2: The Fe-rich corner of the isothermal section at T=1073°C.
Table 6.2: Cr contraction in each phase at the selected temperatures

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Phases</th>
<th>$C^\gamma_{\text{Cr}}$ or $C^\alpha_{\text{Cr}}$ (%)</th>
<th>$C^\alpha_{\text{Cr}}$ (%)</th>
<th>$C^\gamma_{\text{Cr}}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>$\alpha + M_{23}C_6$</td>
<td>2.14</td>
<td>94.10</td>
<td>0.00</td>
</tr>
<tr>
<td>573</td>
<td>$\alpha + M_{23}C_6$</td>
<td>2.16</td>
<td>89.60</td>
<td>0.00</td>
</tr>
<tr>
<td>773</td>
<td>$\alpha + M_{23}C_6$</td>
<td>3.9</td>
<td>77.87</td>
<td>0.00</td>
</tr>
<tr>
<td>937</td>
<td>$M_{23}C_6 \leftrightarrow M_{23}C_6 + M_7C_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>973</td>
<td>$\alpha + M_{23}C_6 + M_7C_3$</td>
<td>5.73</td>
<td>64.41</td>
<td>80.51</td>
</tr>
<tr>
<td>1073</td>
<td>$\alpha + M_{23}C_6 + M_7C_3$</td>
<td>7.31</td>
<td>58.95</td>
<td>78.88</td>
</tr>
<tr>
<td>1088</td>
<td>$\alpha \leftrightarrow \gamma$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1157</td>
<td>$M_{23}C_6 + M_7C_3 \leftrightarrow M_7C_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1173</td>
<td>$\gamma + M_7C_3$</td>
<td>9.32</td>
<td>0.00</td>
<td>73.02</td>
</tr>
<tr>
<td>1273</td>
<td>$\gamma + M_7C_3$</td>
<td>10.57</td>
<td>0.00</td>
<td>69.00</td>
</tr>
<tr>
<td>1323</td>
<td>$\gamma + M_7C_3$</td>
<td>11.27</td>
<td>0.00</td>
<td>67.24</td>
</tr>
<tr>
<td>1383</td>
<td>$\gamma + M_7C_3$</td>
<td>12.28</td>
<td>0.00</td>
<td>64.73</td>
</tr>
<tr>
<td>1418</td>
<td>$\gamma + M_7C_3$</td>
<td>12.59</td>
<td>0.00</td>
<td>64.48</td>
</tr>
<tr>
<td>1437</td>
<td>$\gamma$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1448</td>
<td>$\gamma$</td>
<td>13.0</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>1475</td>
<td>$\gamma$</td>
<td>13.0</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>
6.2 Kinetic data

The diffusivity, the carbide/austenite interfacial energy and the equilibrium solubility of chromium need to be obtained for the simulation by the model.

Due to the lack of published data for the alloy of interest, the diffusion data of Cr in γ- Fe for the 13%Cr stainless steel in the temperature range of 1173~1618K was used for the simulation. The commonly recommended chromium diffusion coefficient $D_{cr-o}$ is $0.169 \text{cm}^2/\text{sec}$ and the activation energy is 263900 J/mole. Thus, we obtained that the diffusivity for chromium in the austenite is

$$D_{cr} = 0.169 \exp\left(-\frac{263900}{RT}\right)$$

(6.3)

The energy of the M23C6/austenite interface is another one that is lacking in the literatures. In this study, a constant cementite carbide (Fe₃C) and austenite interfacial energy of 0.000074 (J/cm²) is used for all temperature range. For the M23C₆/austenite, the interface energy might not be the same during the hardening heat treatment and this can result in errors in the numerical calculation.

The molar volume of the carbide $V_m$, which is required by Eqn. 5.59, is a constant and equals to $92.90 (\text{cm}^3/\text{mole})$. The molar volume of Fe₃C was adapted for this study.
6.3 Temperature profile of the austenitization furnace

In order to carry out numerical simulation of the carbide dissolution and coarsening, an austenitization temperature profile is required. The furnace ambient temperatures were measured based on the description of Section 3.3 and the results are shown in Section 4.2. Since the austenitization times, 6 s, 7.5 s, 11.25 s and 18 s, were controlled by four different steel feeding speeds, different heating rates resulted as seen from Figures 4.13 to 4.15. By re-plotting the temperature profile per each individual temperature- and time-setting and the austenitization temperature profile can be described into two parts: 1) the heating stage where the temperature (T) as a function of time (t) can be fitted in a polynomial and 2) the holding stage where the temperature T is constant. Figures 6.2 to 6.6 show the temperature profiles used in the simulation model verification. It should be noted that austenitization temperature “T=1081°C”, “T=1114°C” and “T=1143°C” are the nominal austenitization temperatures since the austenitization temperature profile is not entirely constant.
Figure 6.3: Austenitization temperature profile at $T=1114^\circ C$ and $t=6$ seconds.

Figure 6.4: Austenitization temperature profile at $T=1114^\circ C$ and $t=7.5$ s.
Figure 6.5: Austenitization temperature profile at $T=1114^\circ C$ and $t=18$ seconds

Figure 6.6: Austenitization temperature profile at $T=1081^\circ C$ and $t=7.5$ s.
Figure 6.7: Austenitization temperature profile at $T=1143^\circ C$ and $t=7.5$ seconds.

Table 6.3 summarizes the temperature profiles during austenitization at various austenitization times and temperatures. The information is used in the modeling simulation.

Table 6.3: Summary of the temperature and time during austenitization for each setting

<table>
<thead>
<tr>
<th>Nominal furnace $T$ ($^\circ C$)</th>
<th>Total run time $t$ (s)</th>
<th>Heating time $t$ (s)</th>
<th>Heating $T$-t functions (°C)</th>
<th>Holding time (s)</th>
<th>Holding $T$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1081</td>
<td>7.5</td>
<td>2</td>
<td>$T = -99.317t^2 + 343.6t + 775$</td>
<td>5.5</td>
<td>1081</td>
</tr>
<tr>
<td>1114</td>
<td>6</td>
<td>1.5</td>
<td>$T = -174.19t^2 + 471.87t + 784.75$</td>
<td>4.5</td>
<td>1114</td>
</tr>
<tr>
<td></td>
<td>7.5</td>
<td>2</td>
<td>$T = -104.16t^2 + 356.2t + 805.06$</td>
<td>5.5</td>
<td>1114</td>
</tr>
<tr>
<td></td>
<td>18</td>
<td>4</td>
<td>$T = -20.87t^2 + 165.3t + 782.13$</td>
<td>14</td>
<td>1114</td>
</tr>
<tr>
<td>1143</td>
<td>7.5</td>
<td>2</td>
<td>$T = -109.34t^2 + 404.76t + 762.06$</td>
<td>5.5</td>
<td>1143</td>
</tr>
</tbody>
</table>
6.4 Computing program

Matlab programs were written for the computation with the simulation model that was developed in this study. The program contains 5 modules. Module 1, Get Global Constant, allows input of gas constant $R$ which is 8.314 J/mol-K. Module 2, Get Material, allows input of material initial information including material’s kinetic and thermodynamic data, the initial carbide mean radius and the initial variance of a Gaussian distribution. Module 3, Iterating dissolution and coarsening, computes dissolution and coarsening using Eqs. (5.57), and (5.61) alternately with the input of the austenitization temperature profile, chromium concentration profile and the final radius is calculated. Module 4, Modeling, calculates the variance or standard deviation using Eq. (5.30). Module 5, Gauss distribution, plots the output from module 4 to a Gaussian plot using Eq. (5.2). Table 6.4 lists the parameters used in the modeling calculation.

<table>
<thead>
<tr>
<th>Gas constant R</th>
<th>Constant C in Eq. 5.61</th>
<th>Molar volume $V_m$</th>
<th>Interfacial energy $\gamma$</th>
<th>Diffusivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.314 J/mol-K</td>
<td>8/9</td>
<td>92.90 * (cm$^3$/mole)</td>
<td>0.000074$^{21}$ (J/cm$^2$)</td>
<td>$D_{Cr} = 0.169 \exp(-263900/RT)$</td>
</tr>
</tbody>
</table>

*Molar volume of Fe$_3$C is used

With the initial input of $r_0$ which is obtained from the raw material characterization, input of chromium concentration as described in Section 6.1 and the selected incremental time $\Delta t_1 = 0.35$ s which also determines the temperature T based on the temperature profile as listed Section 6.3, $\Delta r_{11}$, the radius dissolution for the first 0.35 seconds, can be calculated using Eq. 5.57. With the
input of \( r_{i1} \) which is \( r_0 \) minus \( \Delta r_{i1}, \Delta r_{i2} \), the radius coarsening for the first 0.35 seconds, can be calculated using Eq. (5.61). Then \( r_{i2} (=r_{i1}+\Delta r_{i2}) \) will be used as the input to calculate \( r_{21} \) which is the radius after the dissolution for the second 0.35 seconds using Eq. 5.57 and then \( r_{22} \) can be calculated and so and so forth. Forty (\( n=40 \)) iteration steps were conducted in this study. The variance is calculated using Eq. (5.30) with the input of initial variance from the raw material characterization and the \( \Delta x \) from the above mentioned iteration. With the output of radius and variance, the volume fraction and amount of carbide dissolution can be calculated using Eqs. (5.37) and (5.38).

The program applies not only to the different heat treatment settings, but to different materials by changing material data in the “Get material module”. The detailed programs are attached in Appendix II.
6.5 Modeling Verification

The simulation model, developed in chapter 5, was computed as described in Section 6.4. The calculated results are plotted in Figures 6.7 - 6.12 with comparing to the experimental results and the numerical results are listed in Table 6.4. It was found that the simulated values are in satisfactory agreement with the experimental values in terms of the magnitude and the trends.

Figure 6.8 shows the calculated Gaussian distribution of carbide particle radius after austenitization for 7.5 seconds at the nominal temperatures of 1081°C, 1114°C, and 1143°C respectively. With increasing austenitization temperature, the Gaussian curve is supposed to shifts to the left and the variance also decreases as Gauss curve becoming skinnier. However, the differences are too small to be visible on the plot. The numerical differences can be seen in the Table 6.5.
Figure 6.8: The calculated Gauss distribution at various nominal austenitization temperature, (a) austenitizing at 1081°C for 7.5s, b) austenitizing at 1114°C for 7.5s, and (c) austenitizing at 1143°C for 7.5 s.

Figure 6.9 shows the calculated Gaussian distributions of austenitizing for 6 s, 7.5 s and 18 s at 1114°C respectively. With increasing austenitization time, the Gauss peak is supposed shifts to the left and the variance also decreases indicate more carbide had been dissolved. However the difference is quite small to be seen on the plots. The numerical differences are listed in the Table 6.5.
Figure 6.9: The calculated Gaussian distribution at various austenitization time, (a) austenitizing for 6 s at nominal 1114°C, (b) austenitizing at for 7.5 s at nominal 1114°C, and (c) austenitizing for 18 s at 1114°C.

Figures 6.10 and 6.11 indicate that the calculated and measured mean radii are in reasonable agreement in terms of variation trends, although the simulation values are slightly lower, and also found in somewhat decrease with increase austenitizing temperature, which the experimental values somewhat increases. This suggests that dissolution has stronger effects on the mean radius than coarsening in the simulation, while coarsening has stronger effects in reality. Nonetheless, the overall agreement between the simulation and experimental data seems to validate the usefulness of the simulation model.
Figure 6.10: The calculated and experimental radii vs. austenitization temperature for Steel B austenitizing for 7.5 seconds.

Figure 6.11: The calculated and experimental radii vs. austenitizing time austenitizing at 1114°C.
Figures 6.12 and 6.13 compare the simulated and measured amounts of the carbide dissolution in volume percentage at different austenitization temperatures and times, respectively. In both plots, the simulated values fall behind the measured values, while they both increase with increasing austenitizing temperature and time, which is expected. The lower values of carbide dissolution predicted by the model may reflect the use of 2D radius values in the model which is based on 3D radius. Since in 2D mean radius is less than the 3D mean radius by 18.4%, the model is fed with initial radius values smaller than the actual, which could reduce simulated percentage dissolution by as much as 45%. Future work is necessary to address the 2D verses 3D conversion of either input or calculation results.

Figure 6.12: The calculated and experimental carbide dissolution verses austenitization temperature with fixed austenitizing time for 7.5 seconds.
Figure 6.13: The calculated and experimental carbide dissolution verses austenitizing time at fixed austenitizing temperature of 1114°C

Table 6.5 shows that the calculated radius, variance, volume fraction and the amount of carbide dissolution are in a satisfactory agreement (the same magnitude) with the experimental results for each of the heat treatment settings. The deviations may be attributed to the assumptions and simplifications made in this study due to the lack published data for this particular material.
Table 6.5: The comparison of experimental data and calculated data

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Total time (s)</th>
<th>Data Type</th>
<th>Mean Radius (µm)</th>
<th>Standard deviation (σ)*</th>
<th>Variance (σ²)*</th>
<th>Amount of Dissolution (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealed</td>
<td>1081</td>
<td>Experiment</td>
<td>0.1781</td>
<td>0.8093</td>
<td>0.6549</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Experiment</td>
<td>0.1725</td>
<td>0.6550</td>
<td>0.4290</td>
<td>40.20</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Calculated</td>
<td>0.1674</td>
<td>0.8087</td>
<td>0.6540</td>
<td>22.54</td>
</tr>
<tr>
<td></td>
<td>1114</td>
<td>6</td>
<td>Experiment</td>
<td>0.1840</td>
<td>0.6239</td>
<td>0.3893</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Calculated</td>
<td>0.1645</td>
<td>0.8083</td>
<td>0.6533</td>
<td>28.15</td>
</tr>
<tr>
<td></td>
<td>1143</td>
<td>7.5</td>
<td>Experiment</td>
<td>0.1987</td>
<td>0.6519</td>
<td>0.4250</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Calculated</td>
<td>0.1627</td>
<td>0.8084</td>
<td>0.6535</td>
<td>31.13</td>
</tr>
<tr>
<td></td>
<td>1143</td>
<td>18</td>
<td>Experiment</td>
<td>0.1940</td>
<td>0.6291</td>
<td>0.3957</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Calculated</td>
<td>0.1534</td>
<td>0.8087</td>
<td>0.6540</td>
<td>45.42</td>
</tr>
<tr>
<td></td>
<td>1143</td>
<td>7.5</td>
<td>Experiment</td>
<td>0.2019</td>
<td>0.6767</td>
<td>0.4580</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Calculated</td>
<td>0.1576</td>
<td>0.8080</td>
<td>0.6529</td>
<td>39.74</td>
</tr>
</tbody>
</table>

Note: * indicates the sigma is for the Gaussian distribution

Overall the simulation model agrees with the experimental results. The mean radius and the variance which is related to the full width at half maximum of the carbide distribution curve shows a very good agreement between the simulated data and the experimental data in terms of magnitude and the trends.

Within the same magnitude, the simulated radii are slightly lower than the experimental results, while the simulated variance (σ²) is slightly higher than the experimental value. The 2D carbide size simplification is believed to be the main reason for this discrepancy because the measured carbide size on a polished planar surface is always smaller than the carbide maximum radius. The simulated variance is higher than the experimental results, and found to be very close to the initial variance at the annealed state. This indicated that the calculated coarsening is smaller than the actual coarsening. The low diffusivity data might be the issue for the variance discrepancy.
Lack of actual steel austenitization temperature profile can also cause error although this can be very minor. The past experimental data showed that there was no difference in temperature during holding period, but there was a deviation between the strip temperature and the furnace ambient temperature during the heating period although the gap was very small. All those mentioned error sources can cause the discrepancy between the simulated output and the observed data from the experiment.
7. Conclusions

The dissolution and coarsening kinetics of the secondary carbide in a 13 wt.% Cr martensitic stainless steel during austenitization were investigated to optimize the hardening of the stainless steel for both downstream steps and final product quality. The temperature and time for austenitization were the process parameters. Computer-assisted image analysis was employed to determine the carbide size distribution for the stainless steel in the as-received (annealed) and hardened states.

It is found that the amount of retained austenite increases with increasing mean carbide radius. The hardness of the hardened steel increases with increasing % carbide dissolution up to about 5% and decreases above 5% of carbide dissolution, while the retained austenite initially decreases slightly but increases with increasing carbide dissolution.

The carbide particles were found to exhibit a Gaussian size distribution when plotted against the natural log of carbide radius in both as-received and hardened states. Based on the Gaussian distribution of the carbide particles in the martensitic stainless steel, a mathematical simulation model was developed with account for metallurgical kinetics for the prediction of the concurrent dissolution and Ostwald ripening of the secondary carbide particles during austenitization. With inputs of initial carbide size distribution, the model outputs the final carbide size distribution, as well as the total carbide volume dissolution for any imposed heating schedule.

Comparison of simulated distributions with experimental results indicates that both dissolution and coarsening indeed occur concurrently during the hardening process. It was found
that during austenitization the average radius of carbide particles increases quickly as small carbide particles dissolve in the austenite, but increases only slowly once small particles have disappeared. The nearly constant carbide radius maintained after the disappearance of small particles reflects comparable rates of carbide dissolution and coarsening. The cumulative amount of carbide dissolution increases while the average radius remains nearly constant.

Based on the correlation of the hardness and retained austenite with the mean radius and the carbide size distribution as described in Section 4.3, the simulation model helps to optimize heat treating conditions for the mechanical properties desired for downstream manufacturing steps and the final product.
APPENDIX - MATLAB programs for austenitizing at 1114°C for 7.5 seconds

The calculating program has 5 modules.

Module 1 – Get Global Constants

```matlab
function [ constants ] = GetGlobalConstants()
%GETGLOBALCONSTANTS
    constants.R = 8.314   ;  %ideal gas number
end
```

Module 2 – Get Materials

```matlab
function [ material ] = GetMaterial( name )
%GETMATERIAL
    if (strcmp(name,'steel') == 1),
        material.r0=1.7808e-05  ;  %initial carbide radius
        material.delta0 = 0.35;      % 1114 x 7.5s
        material.Q = -263900;        % Activation energy
        material.D0 = 0.169;         %diffusion coefficient
        material.Cinf = 2.14;        % infinity concentration
        material.C = 0.9;            %constant
        material.Gam = 0.000074;     % energy of particle-matrix interface
        material.X = 92.20;          %molar volume of the solute
        material.S0 = 0.80928  ;    %initial width
    end;
end
```

Module 3 - Iterating Dissolution and Coarsening

```matlab
function [ r1, r2 ] = IterateDissolutionAndCoarsening( n, T1, t1, material, constants )
%ITERATEDISSOLUTIONANDCOARSENING
% r0=1.7808e-05  ;  %initial grain size
    r1 = []; r2 = []; if (n <= 0), return; end;

    r1 = zeros(1,n);
    r2 = zeros(1,n);
    r1 = ones(1,n);
```
r2 = ones(1,n);
r0 = material.r0;
r1(1) = material.r0; %dissolution initial grain size
r2(1) = material.r0; %coarsening initial grain size

if (n <= 1), return; end;

delt = material.delta0;

Q = material.Q;% Activation energy
R = constants.R;  %ideal gas number
D0 = material.D0; %diffusion coefficient
Cinf = material.Cinf; % infinity concentration
C = material.C;
Gam = material.Gam; % energy of particle-matrix interface
X0 = material.X;  %equilibrium solubility of the solute

for i=2:n,
    t= i*delt;     % time interval
    if t>t1, return; end;
    if i <= 5,
        % T = -104.16t^2 + 356.2t + 805.06; 1114c X 7.5s; when n=5 Tc=1109
        Tc = (-104.16)*(t*t)+ 356.2*(t)+ 805.06;
        % T = -20.87t^2 + 165.3t + 782.13; 1114c X 18s; when n=11 Tc=1109
        % Tc = (-20.87)*(t*t)+ 165.3*(t)+ 782.13;
        % T = -174.19t^2 + 471.87t + 784.75; 1114c X 6s; when n=4, Tc=1104
        % Tc = (-174.19)*(t*t)+ 471.87*(t)+ 784.75;
        % T= -109.34t^2 + 404.76t + 762.06; 1143c X 7.5s; when n=5, Tc=1136
        % Tc = (-109.34)*(t*t)+ 404.76*(t)+ 762.06;
        % T = -99.317t^2 + 343.6t + 775 ; 1081c X 7.5s; when n=5, Tc=1072
        % Tc = (-99.317)*(t*t)+ 343.6*(t)+ 775;
        T = Tc + 273;  % temperature changes with n
    elseif i > 5,
        T = T1;
    end;

    % if isequal(T,T1), return; end;
    % if T>T1, T=T1; end;

    Cgam = 7*(10^-6)*(T^2)-0.003*T+1.9867  ;
    Ck = 4*(10^-5)*(T^2)-0.1344*T+178.56  ; % the tie-line solute concentraton
    alfa = (Cgam-Cinf)^2/((Ck-Cgam)*(Ck-Cinf))   ; % rate constant
    D = D0*exp(Q/(R*T));
    B = (r1(i-1)-r0)^2+2*alfa*D*delt;
    r1(i) = r0-((r0-r1(i-1)+sqrt(B))/2) ;  %dissolution model  Equation (18)

    X = X0*Cgam*(1/100);
\[\text{delt2} = \frac{(C*D*X*Gam)}{(3*R*T)} \times \left(1/(r1(i)^2)\right) \times \text{delt}; \quad \%\text{coarsening}\]

\[r2(i) = r1(i-1) + \text{delt2}; \quad \%\text{coarsening}\]

\[\text{end;}\]

\[\text{end}\]

**Module 4 – Modeling**

\[\text{n} = 100;\]
\[\text{T1} = 1114 + 273;\]
\[\text{t1} = 7.5;\]

\[\text{constants} = \text{GetGlobalConstants();}\]
\[\text{material} = \text{GetMaterial('steel');}\]
\[\text{[r1, r2] = IterateDissolutionAndCoarsening(n, T1, t1, material, constants);}\]
\[\text{delt} = \text{material.delta0;}\]
\[\% \text{r0 = material.r0;}\]
\[\text{f} = [];\]
\[\% \text{z2 = zeros(1,n);}\]

\[\text{for k=2:n;}\]
\[\quad \text{t} = k*\text{delt;}\]
\[\quad \text{z2} = \log(r2(k-1)*10000);\]
\[\quad \text{s0} = \text{material.S0;}\]

\[\quad \text{if k>1,}\]
\[\quad \quad \text{s} = \sqrt{(s0^2) - \frac{1}{2} \sum \log(r2(k-1)/r1(k-1))};\]
\[\quad \text{end;}\]

\[\quad \% \text{if t >= t1, return; end;}\]
\[\quad \text{if t>=t1, break; end;}\]

\[\text{x} = -5:0.01:0;\]
\[\text{f} = \text{gauss\_distribution(x, z2, s);}\]
\[\% \text{fprintf(1,' iteration= %10d 
',k);}\]

\[\text{end;}\]

\[\text{plot(x,f, 'o');}\]
\[\text{grid on;}\]
Module 5 – Gaussian distribution

function [f]= gauss_distribution(x, z2, s)

    f = []; 
    if (numel(x) == 0), return; end; 
    pai=3.1415926; 
    f = zeros(1,numel(x)); 
    for j=1:numel(x); 
        f(j) = exp(-((x(j)-z2)*(x(j)-z2))/(2*s*s)); 
        f(j) = f(j)/(s*sqrt(2*pai)); 
    end; 
end
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