EFFECTS OF SHORT-TIME TEMPERING ON MECHANICAL PROPERTIES AND
FRACTURE OF 4340 STEEL

by

Virginia K. Judge
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Golden, CO

Date __________________________

Signed: __________________________

Virginia K. Judge

Signed: __________________________

Dr. John G. Speer
Thesis Advisor

Signed: __________________________

Dr. Amy J. Clarke
Thesis Advisor

Golden, CO

Date __________________________

Signed: __________________________

Dr. Angus A. Rockett
Professor and Head
Department of Metallurgical and Materials Engineering
ABSTRACT

Steel is commonly processed via quenching the high temperature austenite phase to form martensite, a microstructure that exhibits high strength with limited ductility and toughness. As-quenched martensite is typically tempered to achieve varying combinations of strength and ductility/toughness, where strength decreases and ductility/toughness increases with higher tempering temperatures and longer tempering times. However, a phenomenon known as tempered martensite embrittlement (TME) produces a decrease in impact toughness at room temperature in the tempering range of 200 to 400 °C for typical tempering times such as 1 hour (3600 s). Tempered martensite embrittlement is also manifested through an increase in the ductile to brittle transition temperature (DBTT). Rapid heating and tempering via induction heating has the potential to improve toughness for tempering temperatures ranging from approximately 500 – 700 °C; however, limited efforts have been focused on applying short-time tempering for high-hardness applications at lower tempering temperatures within the regime of TME. The present work focuses on the effect of rapid tempering on mechanical properties within the TME tempering regime.

Microstructural and mechanical property effects of short-time (1, 10, 100 s) tempering compared to conventional (3600 s) tempering at equivalent tempering parameters are investigated in the present study. Toughness results indicate an improvement in both ductile-to-brittle transition temperature and room temperature toughness with decreasing tempering time at an equivalent tempering parameter. In addition to overall improved toughness, the TME “trough” is observed to diminish with short time tempering when compared to longer tempering times within an equivalent tempering parameter regime. Tensile tests reveal decreased yield and tensile strengths, and increased reductions of area for shorter tempering times within an equivalent tempering parameter regime. When comparing the same strength level, the trends of increasing room temperature impact toughness and increasing reduction of area with shorter tempering times remain applicable. The observed changes in properties suggest that short-time tempering may offer the potential for desirable strength-toughness combinations.

Some time-temperature combinations utilized in the present study fall within regions where tempering stages overlap, or regions where the classical tempering stages (i.e. stage I, II, and II) may operate out of sequential order when iso-tempering curves are considered in the context of characteristic diffusion distance calculations. Greater diffusion distances are shown to be associated with longer tempering times at a given tempering parameter (for mechanisms associated with stage I and II tempering) when tempering parameter and characteristic diffusion distance are compared. Hardness is not a complete indicator of time-temperature equivalence, and additional fundamental understanding of time-temperature relationships is needed to describe microstructures and properties produced by quenching and tempering (Q&T).
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In memory of my father, Dr. Ricky L. Judge
CHAPTER 1
INTRODUCTION

Steel is commonly processed via quenching the high temperature austenite phase to form martensite, a microstructure that may exhibit high strength and low ductility/toughness. As-quenched martensite is typically tempered to achieve a range of strength and ductility/toughness combinations, where strength decreases and ductility/toughness increases with higher tempering temperatures and longer tempering times. However, a phenomenon known as tempered martensite embrittlement (TME) produces a decrease in impact toughness at room temperature in the tempering range of 200 to 400 °C for a tempering time of 1 hour. Tempered martensite embrittlement is also manifested through an increase in ductile to brittle transition temperature (DBTT) [1].

Austenite decomposition, cementite precipitation, and cementite coarsening have all been identified as mechanisms contributing to TME [2–6]. While there are differing opinions on the specifics of the underlying mechanisms of TME, it is generally accepted that cementite formation plays a large role in the observed embrittlement. The most commonly adopted cause of TME involves the decomposition of retained austenite to ferrite and cementite during the second stage of tempering. Upon quenching from austenitizing temperatures, martensite is formed and thin, interlath austenite is often retained. During tempering, retained austenite decomposes to form cementite and ferrite, and this interlath cementite provides preferred crack initiation sites and propagation pathways.

Rapid heating and tempering via induction heating has been suggested to refine and disperse carbide particles, as compared to traditionally tempered microstructures [7–10]. The change in carbide size and distribution allegedly improves toughness properties for tempering temperatures ranging from approximately 500-700 °C [7–10]. Both faster heating rates and shorter holding times during tempering have been proposed to improve impact toughness within the explored tempering temperature ranges (500-700 °C); however, limited efforts have been focused on applying short-time tempering for high-hardness applications at lower tempering temperatures within the regime of TME [11]. With different potential mechanisms operating at lower tempering temperatures, it is of interest to examine the effects of short-time tempering on microstructural and mechanical behavior at low tempering temperatures and within the TME regime. Furthermore, there is opportunity for better understanding of the relationship between short-time tempering, cementite behavior, mechanical properties, and tempering stages.

In this study, the mechanical and microstructural behavior resulting from short-time tempering within the TME regime is evaluated at an equivalent tempering parameter and constant heating rate. A Gleeble 3500 thermo-mechanical simulator is used to perform induction simulation heat treatments at high heating rates, while conventional heat treatments are conducted in salt baths to simulate relatively
slow heating and longer tempering times. Mechanical properties are evaluated through Charpy impact toughness and tensile testing. Microstructural evolution in relation to retained austenite is observed through x-ray diffraction (XRD), while fractography is studied utilizing scanning electron microscopy (SEM) and optical imaging.
2.1 Tempering Stages

Tempering is a process often applied to high strength martensite. The process of tempering produces a tempered martensite structure that is tougher and more ductile, yet lower in strength, than as-quenched martensite. There are three fundamental stages of early tempering in carbon steels that are identified as:

- **Stage I:** The formation of transition carbides, epsilon carbide (or eta carbide), and the lowering of the carbon content of the matrix martensite to about 0.25 wt. %;
- **Stage II:** The transformation of retained austenite to ferrite and cementite;
- **Stage III:** The replacement of transition carbides and low-carbon martensite by cementite and ferrite [1].

These stages occur at varying temperature ranges that may overlap, depending upon tempering times and alloying. The temperature ranges generally accepted for the three stages are 100-250 °C, 200-300 °C, and 250-350 °C for stages I, II, and III, respectively [12]. It should be noted that these temperature ranges typically assume a tempering time of 1 hr.

The “instability” of martensite and driving force for changes during tempering is attributed to carbon supersaturation, retained austenite, and strain energy within the lattice. During the first stage of tempering, carbon supersaturation provides the driving force for carbide formation. The first stage is often preceded by carbon segregation to dislocations and boundaries, as well as carbon clustering [13, 14]. Following the segregation of carbon, eta and/or epsilon carbides form and the martensite matrix carbon content decreases to approximately 0.25 wt. % C (assuming that the as-quenched martensite C level is greater than 0.25 wt. %). The first stage of tempering is recognized as being controlled by the diffusion of carbon through the martensitic matrix [15].

During the second stage of tempering, retained austenite transforms to ferrite and cementite, and the kinetics of austenite decomposition is associated with the activation energy for carbon diffusion in austenite [1]. Figure 2.1 illustrates the fraction of retained austenite and cementite in relation to tempering temperature in 4340 and 4140 steels. Retained austenite begins to decompose at approximately 200 °C, while cementite becomes predominant at roughly 300 °C.
The third stage of tempering involves the replacement of transition carbides and low carbon martensite with cementite and ferrite. The activation energy is similar to that of iron self-diffusion in ferrite \[17\]. As tempering temperatures increase into the range of 500 – 650 °C, secondary hardening can occur through the formation of alloy carbides \[18\], and recovery and recrystallization mechanisms dominate.

2.2 **Time-Temperature Equivalence**

Since tempering is a diffusion assisted process, time and temperature are important variables to consider. In order to obtain similar properties for different tempering processes, time-temperature relations must be understood. In 1945, Hollomon and Jaffe worked on relating time and temperature equivalencies for steels \[19\]. Their work produced what is known as the Hollomon-Jaffe tempering parameter, which relates tempering time and temperature to relative hardness, and is expressed as:

\[
\text{Hardness} = f(T(\log t + c))
\]

\[
\text{Tempering Parameter} = T(\log t + c)
\]

(2.1)

where \(T\) is absolute temperature, \(t\) is time, and \(c\) is a constant related to the steel used. While this method is typically accepted for determining time-temperature equivalence, there has been some speculation regarding the constant \(c\). While Hollomon and Jaffe first stated that \(c\) only varies with carbon content, later studies reported an inconsistency in \(c\)-values for equivalent carbon contents \[20\]. Roberts, Grobe,
and Moersh eventually settled on an averaged c-value to calculate the tempering parameter. Grange and Baughman also conducted a study in which the c-value varied largely with hardness values. Rather than averaging, a c-value was chosen that presented the least amount of scatter in the data [21]. Additional information and analysis concerning the impact of c-value is located in Appendix A.

In 2009, Thomas et al. strove to reevaluate the accuracy of using the tempering parameter equation, and proposed a new method of assessing time-temperature relations using the characteristic diffusion distance [22]. The derivation of the Hollomon-Jaffe equation requires a constant c-value; however, there are significant variations in the c-values presented in many studies, including Hollomon and Jaffe’s original paper [19–21]. This suggests that the tempering parameter may not be the best method of evaluating time-temperature equivalence. The use of the characteristic diffusion distance proved to be a viable alternative for relating time and temperature. The characteristic diffusion distance is represented as:

\[ x_c \approx \sqrt{2Dt} \]  \hspace{1cm} (2.2)

where \( t \) is time and \( D \) is diffusivity given by the equation:

\[ D = D_0 e^{-\frac{Q}{RT}} \]  \hspace{1cm} (2.3)

where \( D_0 \) is the pre-exponential frequency factor, \( Q \) is the activation energy for diffusion, \( R \) is the universal gas constant, and \( T \) is the absolute temperature. The activation energy and pre-exponential factor depend on the type of diffusion that occurs in each tempering stage. For example, Stage I involves the formation of carbides and is dependent on the diffusion of carbon through martensite. Iso-tempering curves were created using the characteristic diffusion distance and suggest the possibility of several tempering stages operating simultaneously, or even out of regular order, when short times are considered. The different regimes determined using the characteristic diffusion distance are displayed in Figure 2.2, where the overlap of stages is clearly observed at short times.

### 2.2.1 Tempering Parameter Applicability to Short-Time Tempering

As the tempering parameter is central to the present study, it is of interest to investigate the applicability of the tempering parameter to short-time tempering. The applicability of the tempering parameter to short-time tempering was considered by Libsch and Powers [23], as well as Semiatin et al. [24].
In the Libsch and Powers study, short time tempers of 5 and 60 s were conducted using induction heating, while 3600 s tempered specimens were heated in a furnace. Temperature was monitored via thermocouples welded to the surface of the specimen, and temperatures were claimed to be accurate within ~10 °C. During tempering, all induction heated specimens were heated at a rate of approximately 150 °C/s and water quenched. It is unclear in the paper as to when hold times were initiated: upon reaching the desired temperature or upon heating. The hardness of each tempering condition was then measured and compared to the equation for predicting tempered hardness [19]:

\[
R_c = H_c - 0.00457 \times T(13 + \log(t))
\]  

(2.4)

where \(R_c\) is hardness in Rockwell C, \(T\) is the absolute tempering temperature, \(t\) is the tempering time in seconds, and \(H_c\) is the indicated hardness when the tempering parameter \(T(c+\log(t))\) is extrapolated to zero. It should be noted that Libsch and Powers present Equation 2.4 in terms of Rankine for temperature, giving a slope of -0.00254. The version of Equation 2.4 presented here can be found in the original time-temperature equivalence study by Hollomon and Jaffe [19]. Figure 2.3 displays the small deviation of the experimental hardness values from the predictions, calculated using Equation 2.4 [19]. The general deviation of the curves is attributed to true tempering curves never precisely following the Hollomon-Jaffe relation and to some resistance to softening in low alloy steels.
Figure 2.4 displays the results from a short-time tempering study conducted by Semiatin et al [24]. In this study, specimens were heated utilizing salt pots. Specimens were 0.25 cm thick, thin enough to ensure through-heating during salt pot tempering and thick enough to accommodate Rockwell C hardness measurements, as claimed by the authors. It was determined that heating to the tempering temperature typically required between 3 and 5 seconds, therefore hold-time was initiated approximately 4 seconds following submersion in the at-temperature molten salt. Figure 2.4 displays Rockwell C hardness in relation to the Grange-Baughman tempering parameter. The Grange and Baughman parameter takes on much the same form as that of the Hollomon and Jaffe parameter, yet includes effects that alloying elements may have on softening. As exhibited in Figure 2.4, the experimental hardness values correspond well with the Grange and Baughman (G&B) predictions. Furthermore, both short (6 s) and relatively long (60 and 600 s) tempering times exhibit consistent hardness behavior along the same trendline. The largest deviation in hardness behavior between the experimental and G&B predictions is associated with alloy 1020. The authors attribute this hardness deviation to residual amounts of nickel, chromium, and molybdenum present in the experimental alloy that is not normally found in 1020 steels. The authors re-calculate the G&B parameter to include these
alloying additions and show a much better agreement between the experimental and predicted hardness values for alloy 1020.

The results presented in Figure 2.3 and Figure 2.4 indicate that the Hollomon-Jaffé tempering parameter is helpful for equating tempering processes using hardness, even for rapid time conditions. Both studies by Libsch and Powers and Semiatin et al. were based solely on the resultant hardness of the short-time tempered material. Tensile properties, impact toughness, and microstructural characteristics were not a focus of these studies; these aspects represent an important focus of the current work.

![Figure 2.4 Iso-tempering curves of experimental data from Semiatin study compared to Grange and Baughman predictions. Adapted from [24].](image)

### 2.2.2 Isothermal Tempering Equivalence – Contributions from Heating/Cooling

As discussed in section 2.2, the Hollomon-Jaffé tempering parameter relates time and temperature to hardness to provide a method for determining equivalent degrees of tempering for various tempering conditions. This relationship has proven to be fairly accurate when applied to sufficiently long holding times, where the heating and cooling experienced during the tempering process contribute little to overall tempering. While section 2.2.1 showed the tempering parameter to be applicable to short-time tempering, it may be necessary to also account for the tempering that occurs during heating and cooling. Semiatin et al. [24] proposed a method for the development of a tempering parameter applicable to non-isothermal tempering that will be used in this study. Figure 2.5 graphically displays the method of equating a non-isothermal tempering cycle to an isothermal cycle. In this representation, the tempering behavior is considered “additive” and thus the tempering parameter is numerically integrated over short “isothermal” time steps. This is accomplished by equating the tempering parameters of each process:
\[ T_i(c + \log \Delta t_i) = T^*(c + \log \Delta t^*) \] (2.5)

where \( c \) is the c-value and \( T^* \) and \( t^* \) are the temperature and time, respectively, of the equivalent isothermal tempering cycle. \( T^* \) is typically equivalent to the peak temperature of the non-isothermal cycle. The time of the equivalent isothermal cycle, \( t^* \), can be determined by solving for \( \Delta t^* \) at each increment of the cycle and then summing all \( \Delta t^* \) values.

![Figure 2.5 Transformation of non-isothermal cycle to isothermal cycle. Adapted from [24].](image)

**2.3 Tempered Martensite Embrittlement (TME)**

Tempered martensite embrittlement is a phenomenon typically characterized by a decrease in room temperature toughness of medium-carbon steels tempered between 200 and 400 °C, as depicted in Figure 2.6 for a 4340 steel [1]. The depth of the toughness trough is often used as a method of determining the severity of embrittlement. It is generally accepted that cementite and retained austenite play central roles in the manifestation of TME; however, there is some discussion regarding the specifics as to how cementite and retained austenite contribute to TME. Discussions within the literature regarding the role of cementite and retained austenite are reviewed here, with a special emphasis on the suggested effects of austenite decomposition, cementite precipitation, and cementite coarsening on TME.
The reduced toughness upon tempering between 200 and 400 °C was first proposed to be associated with the thermal decomposition of interlath retained austenite films to cementite by McMahon and Thomas [26]. Thomas [27] later observed that at a 200 °C tempering temperature, the fracture mode for several medium carbon, chromium containing steels can be described as dimpled rupture; while at 300 °C, the fracture mode transitions to mainly quasi-cleavage. The transition in fracture behavior, as well as the accompanying toughness drop, was found to directly correlate with the temperature range associated with the decomposition of retained austenite upon tempering.

Horn and Ritchie [3] found the severity of TME in both a 4340 and a 300-M steel to directly relate to the volume fraction of retained austenite present in the as-quenched steel. However, rather than attributing this behavior solely to the thermal decomposition of retained austenite during tempering, Horn and Ritchie proposed that TME is also related to the mechanical decomposition of retained austenite to untempered martensite during deformation and fracture. Figure 2.7 displays the basis for this hypothesis, where the TME regime is compared to retained austenite levels prior to and after loading. Figure 2.7a indicates the onset of TME at approximately 400 °C tempering. As shown in Figure 2.7b, 6 vol % of retained austenite is present after oil quenching, and 4 % is still retained up to 400 °C. It is not until approximately 475 °C that the thermal stability of austenite significantly drops, where retained austenite percentage changes from approximately 4 % at 400 °C, to approximately 1 % at 475 °C tempering. In Figure 2.7b, the mechanical stability of the austenite can be examined by comparing the retained austenite at a given tempering temperature under the various loading conditions. In the as-quenched and 100 °C

Figure 2.6  Impact energy of 4340 steel as a function of tempering temperature for a tempering time of 1 hr. Adapted from [25].
tempered condition, the austenite is unstable, as exhibited by full transformation after 2% strain. Mechanical stability is greatest at 300 and 350 °C, and then drops off sharply at 400 °C. The drop in mechanical stability from 350 to 400 °C is evident by the transition from partial transformation at 350 °C to full transformation at 400 °C after 2% strain. The onset of mechanical destabilization at 400 °C led the authors to conclude that the toughness drop associated with TME (~400 °C in this study) is observed partly as a result of the transformation of retained austenite during deformation.

Horn and Ritchie [3] also linked TME to the formation of cementite during tempering. Epsilon carbide was the most abundantly detected carbide at peak toughness just before the onset of TME for both the 4340 and 300-M steels studied, while cementite was detected as the main carbide within the TME trough region. Additionally, a clear shift of the TME trough to lower tempering temperatures from the 300-M steel to the 4340 steel was noted. This behavior was attributed to the increased silicon level of the 300-M steel, which delays the transformation of retained austenite and of E-carbide to cementite. It is important to note that the two mechanisms outlined by Horn and Ritchie, the mechanical decomposition of retained austenite and the formation of cementite, are strongly interconnected. Retained austenite is destabilized through carbon depletion during the formation of cementite precipitates.

King et al. [28] proposed that TME is not linked to the decomposition, thermal or mechanical, of retained austenite, but instead is related to cementite coarsening. Bhadeshia and Edmonds [6] also supported the theory of cementite coarsening as the mechanism responsible for TME. In one studied alloy (Fe-1.08V-0.25C), the retained austenite was noted using transmission electron microscopy (TEM) to have decomposed completely after tempering at 290 °C; however, the steel was not fully embrittled until 350 °C. This observation supports the authors’ theory that TME is not associated with austenite decomposition and cementite formation, but rather the subsequent coarsening of cementite. It should be noted that Bhadeshia and Edmonds’ conclusion related to cementite coarsening was made based on a small sample size, given the method (TEM) of determining the extent of austenite decomposition for small amounts of retained austenite. Coarser, intralath cementite, rather than retained austenite or fine interlath cementite, was shown to be the controlling mechanism of TME in another studied alloy (Fe-Mo-C) [6].

While many distinct mechanisms related to TME have been explored throughout the literature, it is reasonable to conclude that most are interconnected and play some role in TME. Horn and Ritchie related many of the previously discussed mechanisms to arrive at a fairly comprehensive theory involving the manifestation of TME [3]. Upon quenching from austenitizing temperatures, some amount of interlath austenite is retained, contingent on alloying and processing conditions. Upon tempering, the carbon supersaturated martensite and carbon enriched austenite serve as a source of carbon for cementite nucleation and growth on martensite-austenite boundaries. The interlath cementite then acts as an
embrittling agent by promoting crack initiation and providing preferred crack paths. Simultaneously, as carbides are forming, the retained austenite is being depleted of carbon; thereby reducing thermal and mechanical stability. During deformation/fracture, retained austenite remaining within the microstructure may mechanically transform to fresh martensite. The newly transformed martensite, adjacent to the existing cementite films, will then augment any reduced toughness within the material. Therefore, in accordance with Horn and Ritchie’s theory, TME is primarily dependent on the formation of interlath cementite and also the result of thermal and mechanical decomposition of austenite.

![Graph](image)

Figure 2.7  (a) Impact energy versus tempering temperature (for 300-M) with visible TME region and (b) retained austenite versus tempering temperature for material prior to loading, after 0.2% strain, and after 2% strain. Adapted from [3].

The effect of cementite coarsening on TME is still unclear. Proposed TME mechanisms of austenite decomposition and interlath cementite formation could, theoretically, be events that prelude or accompany the actual controlling mechanism: critical cementite particle size. Considering this theory, TME would occur when cementite, inter- or intra-lath, reaches some critical particle size such that fracture is promoted. The cementite coarsening mechanism is embedded in the previously discussed theories, but emphasizes a critical cementite size at which embrittlement occurs.

2.4  Tensile Properties within the TME Regime

The typical mechanical properties used to identify and characterize TME are Charpy impact toughness or fracture toughness. Within the TME regime, impact toughness decreases with increasing tempering temperature. The extent of the toughness drop, or the trough, is often used to characterize the severity of TME. However, it is important to understand other typical mechanical properties within the
TME regime. Several examples from literature are highlighted in order to illustrate the tensile properties associated with TME.

Hardness, ultimate tensile strength (UTS), and yield strength (YS) are typically expected to decrease with increasing tempering temperature, while ductility usually increases. As previously discussed, toughness decreases within the TME regime. Figure 2.8 illustrates the trend of UTS, YS, reduction of area (RA), and total elongation in relation to tempering temperature for 4340 steel treated for 1 hr. There are no observed irregularities in the trends between 200 and 400 °C, where TME is typically observed. In Figure 2.9, the proportional limit (S₀₂), 0.2 percent off-set yield strength (S₀.₂), and ultimate tensile strength (Sₘₚ) are plotted with respect to tempering temperatures within the TME regime. The proportional limit appears relatively insensitive to tempering temperature; however, S₀.₂ and Sₘₚ both decrease with increasing tempering temperature; however, Sₘₚ decreases more rapidly, as shown in Figure 2.8. In both Figure 2.8 and Figure 2.9, there is a relatively large decrease observed in the work hardening rate between 200 and 300 °C; however, there are no observed irregularities in the expected trends related to YS, UTS, RA, and elongation with tempering temperature that might be related to TME.

![Figure 2.8](image)

Figure 2.8 Ultimate tensile strength (UTS), yield strength (YS), elongation (elong.), and reduction in area (RA) with respect to tempering temperature for 4340 steel tempered 1 hr. Adapted from [29].
Figure 2.10 displays the mechanical properties following tempering of a 0.2% C steel (1020) [31]. Contrary to the previous data presented in Figure 2.9, the effect of TME is detected in the reduction of area and elongation data. This behavior is less usual, as TME is typically only detected in Charpy impact data, or reduction of area data at subzero testing temperatures. It is interesting to note that the decrease in elongation or reduction of area occurs in the same tempering range as the peak elastic limit.

Figure 2.10 displays the mechanical properties following tempering of a 0.2% C steel (1020) [31]. Contrary to the previous data presented in Figure 2.9, the effect of TME is detected in the reduction of area and elongation data. This behavior is less usual, as TME is typically only detected in Charpy impact data, or reduction of area data at subzero testing temperatures. It is interesting to note that the decrease in elongation or reduction of area occurs in the same tempering range as the peak elastic limit.

Figure 2.10 Elongation, RA, and stress versus tempering temperature. Typical TME regime is highlighted. Adapted from [31].
2.5 Fracture

Fracture is the process of a solid body separating during the application of stress [32], and is often classified as either ductile or brittle. Ductile fracture involves plastic deformation during the formation and propagation of a crack, while brittle fracture exhibits little plastic deformation and a rapid rate of crack propagation. The microstructural properties that control the ease of ductile and brittle fracture are discussed in this section. The theory of the ductile to brittle transition temperature is also discussed.

2.5.1 Ductile Fracture

Ductile fracture is primarily attributed to the formation, growth, and subsequent coalescence of voids [33]. Void nucleation typically occurs at second phase particles, although voids have also been observed to form at interfaces and slip band intersections [34–37]. Following nucleation, voids begin to grow with morphologies influenced by material properties and test conditions. Void coalescence occurs when voids link together as a result of growth. Ductile fracture is typically characterized by distinct, sequential stages of void nucleation, growth, and coalescence. As discussed above, these stages often occur simultaneously, and the distinction between stages is not always clear.

Void nucleation has been shown to be a function of second-phase particle size, stress state, matrix strength, particle-matrix cohesion, and impurity atom concentration to particle-matrix interfaces [38–41]. Through studies involving a range of materials, it has been concluded that voids tend to nucleate first at larger, second-phase particles; therefore, larger particles are expected to nucleate voids at lower strains [38–40, 42]. A matrix with a small particle size distribution requires a higher strain to initiate void nucleation, compared to a matrix containing relatively large particles. Stress state was shown to affect void nucleation by Cox and Low, where notched specimens with a higher degree of triaxiality exhibited void nucleation at lower strains than in smooth specimens [39]. Finally, void nucleation has been observed to occur at lower strains with increasing matrix strength and high impurity concentration at the particle-matrix interface [38, 41]. Conversely, higher strains are required as the strength of bonds at the particle-matrix interface increases.

Like the nucleation process, void growth is affected by a number of factors including: strain rate, strain hardening rate, matrix strength, and stress state. An increase in strain rate amplifies the growth rate; while, for a given strain rate, an increase in strain hardening rate decreases void growth rates. Much like nucleation, void growth increases with matrix strength and the degree of triaxiality [39, 43].

The final stage of ductile fracture, void coalescence, occurs after voids impinge. If there is one prominent second-phase particle at which voids form, coalescence will occur upon the meeting of voids. This type of coalescence is often referred to as direct impingement. Conversely, if there are two void nucleating second-phase particle types within the matrix, voids will first form at the particles with a
weaker particle-matrix bond interface or bigger particles with a higher stress concentration. Later during the deformation process, when strains are sufficiently high, void nucleation will occur at more strongly bonded, often smaller, particles. The voids at the smaller particles then act as links to the larger surrounding voids in a process often described as void sheet coalescence. It was shown by Moody and Greulich that a second particle population is not necessarily required for the process of void sheet coalescence to occur [44]. Instead, microvoids may also form at locations such as grain boundary carbides and slip bands.

2.5.2 Brittle Fracture

There are multiple proposed models for brittle cleavage nucleation; one such model claims that brittle cleavage fracture can be characterized by three stages:

- The pile-up of dislocations at an obstacle along a distinct slip plane
- The accumulation of shear stress at the head of the pile-up, leading to the coalescence of dislocations and formation of a microcrack
- Extension and propagation of the microcrack, initiated by an increase in stress. In some cases, the microcrack can propagate without the introduction of additional stress through stored elastic energy, although an increase in stress is more typically required [32].

Figure 2.11 illustrates the formation of a microcrack at an edge dislocation pile-up. The dislocations within the pile-up are pushed so closely together that at some critical stress the dislocations coalesce and create a wedge microcrack [45]. The process illustrated in Figure 2.11 can be represented by the relationship:

\[(\tau_s - \tau_i)nb \approx 2\gamma_s\]  

(2.6)

where \(\tau_s\) is the applied shear stress, \(\tau_i\) is the frictional shear stress, \(n\) is the number of dislocations, \(b\) is the burgers vector, and \(\gamma_s\) is the surface energy. Equation 2.6 is interpreted such that a crack will form once the applied shear stress associated with the displacement \(nb\) is equal to the sum of the work required to move dislocations against the friction stress and the work done in creating a new surface.

Following crack nucleation, it is possible for crack propagation to occur by plastic deformation if the dislocation source continually produces dislocations to perpetuate pile-up and subsequent opening of the microcrack; however, tensile stresses are typically required for crack propagation to occur. Since brittle fracture has been shown to increase with hydrostatic tensile stress [46], and no tensile stress is required for microcrack formation, it is believed that crack propagation is the controlling step for brittle
fracture. Crack propagation becomes increasingly difficult with the presence of strong barriers, such as grain boundaries [47].

Brittle fracture can be characterized by a singular event involving the occurrence of fracture due to the propagation of a single crack; however, a form of brittle fracture known as quasi-cleavage is not quite as simple. Quasi-cleavage is identified by cleavage facets that are separated by ductile tear ridges and is often observed in tempered martensite [32]. Rather than a singular event causing the onset of fracture, quasi-cleavage occurs from many, frequent crack initiation and propagation events. Cracks arrest at misoriented lath packets or prior austenite grain boundaries. The final, large scale, cleavage event takes place following the initial formation of these many microcracks. This event occurs upon the coalescence of microcracks or ductile tear ridges to produce a single, large crack zone [48].

### 2.5.3 Ductile to Brittle Transition

In steels and other BCC materials, there is a temperature at which a transition from ductile to brittle fracture occurs. One prominent theory describing the origin of this phenomenon was presented by Cottrell with the following equation [49]:

\[
(\tau_i D^{1/2} + k') = G\gamma_s\beta
\]  

(2.7)

where \( \tau_i \) is the resistance of the lattice to dislocation movement, \( D \) is the grain size, \( k' \) is a parameter related to the release of dislocations into a pile-up, \( G \) is the shear modulus, \( \gamma_s \) is the effective surface energy (including the energy of plastic deformation), and \( \beta \) is a term that expresses the ratio of shear to normal stress. The relationship between the two sides of this equation determines the type of fracture that will occur. If the right side of the equation is larger than the left, then microcracks can form, but not
propagate. Conversely, when the left side is larger, crack formation and propagation will occur at a shear stress greater than or equal to the yield stress. Many of the variables within Equation 2.7 are temperature dependent, and there is a critical temperature at which the relationship between the two sides of the equation reverses and fracture transitions from ductile to brittle. This temperature is referred to as the ductile-to-brittle transition temperature (DBTT).

The DBTT of steel can often be affected by alloying and processing. Typically, the effects imposed on the fracture behavior are a result of altering one or more of the variables in Equation 2.7. As the resistance to lattice dislocation movement \( \tau_i \) increases, brittle fracture becomes more prominent, due to the buildup of high stresses prior to or after yielding. Materials with a high \( k' \) are more inclined to brittle fracture, since the rate at which dislocations are released into a pile-up affects the resulting stress of the pile-up. Conversely, materials with a high surface energy and shear to normal stress ratio are typically more likely to undergo ductile fracture at low temperatures. Slip-band length, often associated with grain size, can also have an effect on the mode of fracture. A smaller slip-band length, where dislocations will be impeded more often, promotes ductile fracture at lower temperatures. Other than grain size, particle spacing and dislocation density can also affect slip-band length. In quenched and tempered steel, a finer particle spacing has been observed to shift the ductile-to-brittle transition temperature to lower temperatures [32].

2.5.4 Fractography

Fracture surface morphologies can be helpful in revealing the manner in which fracture occurred. Some of the primary, microscopic features identified include: cleavage, quasi-cleavage, intergranular fracture, and ductile rupture. Cleavage is associated with brittle fracture and is characterized by flat facets that occur along specific crystallographic planes. The size of cleavage facets is often related to ferrite grain size in steels. Quasi-cleavage is similar to cleavage; however, tear ridges and dimples are also present along the edge of the facet planes [32, 50]. Quasi-cleavage is often associated with fracture in quenched-and-tempered steel, where facet size can be related to prior austenite grain size. Intergranular fracture is yet another fracture morphology associated with brittle fracture. Unlike cleavage and quasi-cleavage, where the fracture path is transgranular, the crack path of intergranular fracture runs in between grains.

Ductile fracture is typically recognizable on a microscopic level through the presence of microvoids. Ductile rupture, or microvoid coalescence, is characterized by the formation of cup-like structures. This morphology develops due to the nucleation, growth, and coalescence of voids. Voids form at what later appear to be depressions and subsequently grow. Eventually, the voids grow large enough to where they coalesce, and the filaments separating them fracture.
2.6 Induction Tempering

Conventional tempering involves the use of furnaces and baths to heat using a combination of convection, conduction, and radiation. In contrast, induction tempering uses magnetic fields to generate eddy currents within the material. Heat is generated from the flow of these eddy currents against the resistance of the material’s imperfect conductivity. An illustration of the process of induction tempering is displayed in Figure 2.12. Induction tempering is commonly used for rapid tempering where tempering times are often on the scale of seconds or less, whereas conventional tempering is usually on the scale of minutes or hours [51]. Additionally, induction heating typically involves faster heating rates compared to conventional tempering.

![Figure 2.12 Depiction of induction heating [52].](image)

2.7 Effect of Rapid Heating and Tempering on Mechanical Properties and Microstructure of Martensite

Rapid heating rates and short holding times during tempering have been suggested to improve impact toughness via cementite refinement for high temperature (500-700 °C) tempering conditions [7–10, 53, 54]. At relatively low tempering temperatures, cementite and transitions carbides form due to the supersaturation of carbon. As tempering temperature increases, dislocation annihilation and recovery occurs while cementite undergoes rapid growth. During conventional tempering, heating rates are often slow enough to provide sufficient time for carbon diffusion and dislocation annealing to occur. Due to the apparent limitation of these two factors during rapid heating and tempering, more finely dispersed cementite is said to form compared to conventional tempering at an equivalent hardness level [7–9, 11].

The effect of short-time tempering via induction tempering was first investigated by Nakashima and Libsch [11]. Hardness and impact energies of furnace and induction tempered specimens were
compared. Figure 2.13 displays the results of this study relating the effects of rapid tempering on room temperature toughness with respect to hardness. Tempering temperature ranged from approximately 100-700 °C in this study and 0 s tempering indicates that specimens were immediately quenched once the desired tempering temperature was achieved. Within an equivalent hardness range, it was found that the TME toughness trough “shape” is diminished by rapid heating and tempering; however, room temperature toughness values did not significantly improve. Diminishment of the TME trough shape with short-time tempering is apparent in this data, as there is no observed decrease in impact energy with decreasing hardness (increasing tempering), as is observed for the 1 hr tempering time condition. However, for a given hardness value, short-time tempers do not consistently and significantly exhibit higher impact energy values compared to the conventionally tempered specimen.

Figure 2.13 (a) Room temperature impact energy as a function of hardness (HRC) for tempering times of 1 hr and 0 s. Tempering condition of 0 s indicates that specimens were immediately quenched was the desired tempering temperature was reached. Adapted from [11].

To facilitate our understanding of the relationship between TME trough shape behavior and overall toughness, it is helpful to consider the usual definition of TME. TME is defined as a “drop in room temperature impact toughness as tempering temperature is raised” (or hardness is decreased) [55]. The severity of TME is often characterized by the depth of the toughness trough. Per this definition, as long as the toughness trough is diminished, TME is considered to be diminished. Figure 2.13 exhibits a diminishing of the TME trough shape, but this behavior is accompanied by a decrease in impact
toughness. To better clarify, Figure 2.14 illustrates two ways in which the TME toughness trough shape may be “diminished.” In one instance the overall toughness increases while in the other it decreases.

Figure 2.15 displays the transition temperature results from the Nakashima and Libsch [11] study for specimens tempered to a hardness of approximately 53 HRC. It is shown in Figure 2.15 that transition temperature is lower at an equivalent hardness for the short-time temper (0 s) compared to the conventional temper (1 hr). While transition temperature is improved with short-time tempering, the upper and lower shelf energies are equivalent for the short and conventional tempers.

The behavior observed in Figure 2.13 was attributed to a change in the shape and distribution of cementite with short-time tempering. Nakashima and Libsch observed that the shorter tempering time conditions exhibited finer, more evenly distributed cementite. Furthermore, cementite films associated with the short-time temper took on a more globular morphology than the cementite films associated with the conventional temper. These microstructural comparisons were made at an equivalent hardness level of approximately 53 HRC (360 °C-0 s, 250 °C-1 hr), corresponding to the hardness level employed in the comparison of transition temperature characteristics in Figure 2.15.
After Nakashima and Libsch’s study, most rapid heating coupled with short-time tempering has been conducted at higher tempering temperatures (~500 – 700 °C) than those traditionally associated with TME. An effort toward separating the effect of hold time and heating rate on mechanical properties has been pursued. Nagao et al. performed induction and conventional tempers on low carbon, high strength steels [10]. The induction tempers were performed at heating rates ranging from 0.3 to 100 °C/s to temperatures of 560 – 650 °C for holding times of 10 and 600 s. Conventional heat treatments were conducted in a furnace and assumed to have a heating rate of approximately 0.3 °C/s. Figure 2.16a and Figure 2.16b display the hardness and impact fracture appearance transition temperature (FATT) results associated with the various heating rates explored. Specific details related to holding times and temperatures and FATT determination associated with the data displayed in Figure 2.16 are not reported. Nagao et al. concluded that heating rate, rather than holding time, was responsible for the observed decrease in transition temperature. While improved toughness properties were attributed to faster heating rates in the Nagao et al. study, it seems that there is some heating rate threshold associated with the improvement in transition temperatures displayed in Figure 2.16b. A relatively slow heating rate of 0.3 °C/s exhibits overall higher transition temperatures; however, it is apparent that there is little variation in impact toughness properties for heating rates ranging from 5 to 100 °C/s. Therefore, while the authors attribute improved toughness to faster heating rates, this relationship is only clear when comparing the 0.3 °C/s to 5-100 °C/s results. Conversely, increasing heating rate from 5 to 100 °C/s apparently produces

![Figure 2.15](image-url)  
**Figure 2.15** Impact energy as a function of testing temperature in °C for tempering times of 1 hr and 0 s at an equivalent hardness of approximately 53 HRC. Adapted from [11].
no improvement in toughness. Therefore, there seems to be a critical heating rate (threshold) between the 0.3 and 5 °C/s at which the microstructural development is affected such that toughness is improved.

Kawasaki *et al.* [53] also explored the effects of rapid tempering through induction heating. Specimens were heat treated one of four ways: induction austenitized and induction tempered (II), induction austenitized and furnace tempered (IF), furnace austenitized and induction tempered (FI), or furnace austenitized and furnace tempered (FF). Figure 2.17 displays the toughness characteristics of the variously treated specimens at equivalent hardness values. The combination of induction austenitizing and tempering yielded the best Charpy impact results, while the combination of furnace austenitizing and tempering exhibits the lowest impact toughness values. Like Nagao *et al.*, this study also outlined the role of heating rate in the resultant mechanical properties. Figure 2.18a displays the impact toughness results of a 5 s temper with heating rates of 1 and 100 °C/s. It is evident that, at equivalent hardness values, better impact toughness characteristics are achieved with the faster heating rate. The role of tempering hold time was also explored and is displayed in Figure 2.18b. Shorter hold times, at a constant heating rate and hardness value, are shown to yield superior impact toughness properties.

![Graphs showing mechanical properties vs. tempering parameter](image.png)

Figure 2.16 (a) HV10 (average of Vickers hardness with a load of 98 N (10 kg)) versus tempering parameter and (b) fracture appearance transition temperature (FATT) versus tempering parameter for different heating rates. Adapted from [10].
Many of the previously mentioned studies comment on supposed higher dislocation densities associated with rapidly heated specimens [7–10]. Increased dislocation population, quantitatively shown by Furuhara et al. [7] and Revilla et al. [8], is said to originate from decreased time available for...
dislocation annealing to occur. In slowly heated specimens, there is sufficient time during heating for dislocation recovery and annihilation; therefore, there is a decreased dislocation population available to nucleate carbides. Since the rapidly heated specimens maintain high dislocation densities, this is said to provide additional sites for nucleation and therefore produce more dispersed precipitates. The dislocation density data presented by Furuhara et al. [7] and displayed in Table 2.1 suggest increased dislocation density at a higher heating rate; however, it is evident that there is little change in dislocation density between slowly and rapidly heated samples for a similar tempering parameter. This is due to the corresponding temperature increase required to maintain an equivalent tempering parameter at shorter times. The increase in temperature enables dislocation rearrangement that is otherwise limited by the rapid heating rate. Therefore, it may be of interest to more closely compare the microstructure of specimens that have experienced various heating rates/holding times at similar tempering parameters.

<table>
<thead>
<tr>
<th>Tempering Temperature (°C)</th>
<th>Heating Rate (°C/s)</th>
<th>Tempering Parameter</th>
<th>Dislocation Density ρ x 10^{15} (m^{-2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>550, 0 s</td>
<td>100</td>
<td>11887</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>12710</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>13533</td>
<td>1.5</td>
</tr>
<tr>
<td>650, 0 s</td>
<td>1000</td>
<td>13332</td>
<td>1.5</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>14255</td>
<td>1.6</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>15178</td>
<td>1.1</td>
</tr>
</tbody>
</table>

* Dislocation density determined via TEM using the line-intersection analysis method [56].

In addition to the effects of dislocation density on the nucleation behavior of cementite, Furuhara et al. also related the refinement of cementite particles to time-temperature precipitation kinetics that relate the start of cementite precipitation to heating rate [7]. Figure 2.19a is a schematic of a time-temperature-precipitation diagram and illustrates the suggested effect of heating rate on the temperature at which cementite nucleation occurs. Figure 2.19b schematically displays cementite nucleation rates in relation to temperature for both high-angle grain boundary nucleation and screw dislocation nucleation calculated by Furuhara et al., where it is assumed that the nucleation kinetics are limited by the volume diffusion of carbon (D_C^V). Faster heating rates increase the temperature at which nucleation occurs (Figure 2.19a) and therefore lead to a higher nucleation rate (Figure 2.19b). However, the analysis presented by the authors, indicating that higher nucleation temperatures lead to a higher nucleation rate, is only valid for tempering temperatures ranging from approximately 300 to 500 °C (grain boundary nucleation). For a tempering temperature range of 200 to 300 °C or 500 to 600 °C, increasing the nucleation temperature would lead to a decrease in nucleation rate (dislocation and grain boundary,
respectively). The authors’ focus on temperatures of 300 to 500 °C for the nucleation rate analysis was said to be employed as these temperatures related most closely to the tempering temperatures used in their study; however, this explanation is confusing as the tempering temperatures ranged from approximately 450-650 °C.

An additional explanation regarding the fine, dispersed cementite particles can be linked to the previously discussed dislocation density. With a higher dislocation density, more nucleation sites are available for cementite precipitation, potentially leading to higher nucleation rates and finer, more dispersed particles. The microstructural evolution theories presented by Furuhsara et al. and adopted by others tend to focus on the effect of heating rate, while holding time effects are largely overlooked or not thoroughly explored.

Overall, rapid heating and short hold times during tempering are suggested to limit the opportunity for dislocation recovery and annihilation, therefore producing a more finely dispersed cementite population despite the higher tempering temperatures achieved [7–10]. Rapid tempering at relatively high tempering temperatures (~500-700 °C) has been shown to increase toughness due to the observed changes in cementite distribution [9, 10]. The work of Nakashima and Libsch suggests similar behavior at lower tempering temperatures (~200-500 °C), where improved toughness (transition

Figure 2.19 (a) Time-temperature-transformation diagram illustrating the effect of heating rate on the start temperature of cementite precipitation and (b) temperature versus nucleation rate at dislocations and nucleation rate at grain boundaries. It is assumed that the kinetics are limited by the volume diffusion of carbon through ferrite. Adapted from [7].
temperature) is achieved for shorter tempering times and the TME toughness trough shape is diminished at room temperature.

2.8 Heat Treatment Online Process (HOP)

The combination of rapid heating and tempering is a feasible processing route in plate processing through the implementation of induction tempering. Recently, JFE steel introduced the heat treatment online process (HOP) into commercial production [57]. The HOP utilizes induction heating to rapidly temper material and allegedly produces steels with superior mechanical properties [57–62]. Figure 2.20 illustrates the layout of JFE’s online heat treatment facility.

Literature focusing on the successful implementation of the HOP towards advanced steel-making has outlined many of the same microstructural and mechanical behaviors associated with the rapid heating and tempering literature discussed in section 2.7. In addition to improved impact toughness achieved via rapid heating and tempering, HOP is claimed to improve delayed fracture and formability characteristics through rapid heating [57, 59, 61, 62].

Figure 2.20 Illustration of the heat treatment online process implemented by JFE steel [62].
CHAPTER 3
EXPERIMENTAL DESIGN AND METHODOLOGY

3.1 Experimental Material

AISI 4340 steel was selected due to its susceptibility to TME, as well as its commercial availability and relevance to the proposing sponsor. 4340 has the ability to reach high strength levels, while maintaining ductility and toughness. It is often used for aircraft, structural, and defense applications. The material used for this study has the following composition:

Table 3.1 Chemical Composition of AISI 4340 Research Material (wt pct)

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Nb</th>
<th>V</th>
<th>Al</th>
<th>S</th>
<th>P</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.41</td>
<td>0.71</td>
<td>0.25</td>
<td>1.76</td>
<td>0.75</td>
<td>0.26</td>
<td>0.005</td>
<td>0.047</td>
<td>0.008</td>
<td>0.001</td>
<td>0.009</td>
<td>0.14</td>
</tr>
</tbody>
</table>

The material used for this project was provided by Los Alamos National Laboratory and produced by ArcelorMittal USA. Plate material with a thickness of 12.7 mm (0.5 in) was selected, in order to have sufficient thickness for full-sized Charpy specimens.

3.2 Tempering Matrix

A tempering matrix of times and temperatures was created to explore the TME region for short-time and conventional tempering, and is presented in Table 3.2. Conventional tempering times (1 hr) exhibit TME between 200 and 400 °C; therefore, these temperatures served as a basis for calculating “equivalent” temperatures at shorter times. Iso-tempering curves, displayed in Figure 3.1, were created using the Holloman-Jaffe tempering parameter \( T[\log t + c] \), for a base tempering time of one hour and a c-value of 16. The units of T and t are Kelvin and seconds, respectively. The process used to select the appropriate c-value is outlined in Appendix A. The calculations used to produce Figure 3.1 were consulted to create the tempering matrix displayed in Table 3.2.

Table 3.2 Time-Temperature Tempering Matrix (c = 16)

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3600</td>
<td>200 250 300 350 400</td>
</tr>
<tr>
<td>100</td>
<td>241 295 350 404 458</td>
</tr>
<tr>
<td>10</td>
<td>271 329 386 444 501</td>
</tr>
<tr>
<td>1</td>
<td>305 366 427 489 550</td>
</tr>
</tbody>
</table>
Material Processing – Part I: Charpy Specimens

Charpy blanks were machined from the as-received plate material and then quenched and tempered. Prior to tempering all of the Charpy blank specimens, a preliminary study was performed to ensure that the tempering matrix outlined in section 3.2 would produce similar hardness values for a single tempering parameter, as intended. Following confirmation of the proposed tempering matrix, all Charpy blanks were tempered. Conventional tempering (3600 s) was performed in salt baths, while short-time tempering (1-100 s) was performed using the Gleeble 3500. Following all heat treatments, the Charpy blanks were machined to full-sized Charpy V-notch specimens.

3.3.1 Charpy Blank Geometry

Three of the original 12.7 mm (0.5 in) thick plates were machined into rectangular Charpy blanks, per Figure 3.2. Longitudinal blanks were obtained at the plate mid-thickness. There is 30 mm of available grip contact length in the Gleeble; therefore, the blank was designed to include 30 mm of length on each end of the specimen for gripping. An additional 30 mm was added to provide distance between the two gripped ends. One millimeter was added to the thickness and width of the final Charpy specimen geometry to ensure that any surface effects arising during heat treatment would be removed during final machining. Charpy blanks were marked during machining to denote orientation and provide a reference for final machining of Charpy specimens.
3.3.2 Charpy Blank Austenitizing

The blanks were austenitized at 845 °C for 1 hour and quenched to room temperature with agitated oil. Charpy blanks were hardened at Los Alamos National Laboratory in a vacuum furnace to prevent decarburization. In order to confirm through-hardening, one sample was sectioned for Vickers hardness testing.

The relative cross-section positions for hardness testing with respect to the Charpy blank, as well as the indentation locations for the longitudinal and transverse cross-sections, are displayed in Figure 3.3 and Figure 3.4 respectively. Three measurements were taken per indent and averaged to determine the hardness at each indentation position. Contour maps for the three positions were constructed using the hardness at each indentation position and are displayed in Figure 3.5.

The individual hardness indentation values were averaged to determine the overall average measured hardness, as displayed in Figure 3.6. Hardness measurements from the Charpy blanks ranged from ~52-60 HRC, as indicated by the upper and lower dotted lines in Figure 3.6. According to ASM International, the hardness of fully hardened AISI 4340 can be expected to range between 53 and 60 HRC [63]. The hardness expected for various percentages of martensite is indicated by the data points and corresponding best fit line [64]. The samples were considered to be fully hardened and were approved for further heat treatment, due to the measured hardness values falling within the expected range of fully hardened 4340.
While the blanks were ascertained to be fully hardened, the variation in hardness for a given cross-section should be noted. It is possible, as all Charpy blanks were austenitized and quenched in a single batch, that edges/surfaces directly adjacent to other Charpy blanks experienced decarburization and/or slightly slower cooling rates, resulting in lower hardness values. This is consistent with the hardness trends observed in Figure 3.5, where lower hardness values are observed at locations that correspond to Charpy blank surfaces. However, given that the majority of hardness measurements fell within the expected hardness range (53-60) of fully-hardened 4340, the blanks were considered fully-hardened.

Figure 3.4 Vickers hardness indentation positions for (a) transverse cross-sections corresponding to A and B in Figure 3.3 and (b) longitudinal cross-section corresponding to C in Figure 3.3

Figure 3.5 Transverse hardness contour map for (a) A and (b) B cross-sections. Longitudinal hardness contour map of cross-section (c) C. All axes are in mm and end at an indentation point.
Confirmation of Hardness/Tempering Parameter Relationship

The time-temperature heat treatment matrix, as displayed in Table 3.2, was tested to confirm the applicability of the tempering parameter calculations by performing the appropriate heat treatments and determining the hardness for each condition. Tempering treatments with times of 1, 10, and 100 s were conducted using the Gleeble® 3500, while 3600 s treatments were performed in salt pots. Following tempering, specimens were sectioned and polished according to the ASTM standards for Vickers hardness testing [65]. A matrix of 10-25 Vickers hardness indents was made on each specimen cross-section to determine the hardness corresponding to each time-temperature combination. Vickers hardness was converted to Rockwell C hardness to remain consistent with previously presented literature data (Figure 3.6).

Figure 3.7 illustrates the cross-section position for all Gleeble tempered specimens. Since a temperature gradient, and therefore hardness gradient, is present in all Gleeble tempered samples, accurate positioning of indentations with respect to the thermocouple location was crucial. Further discussion of the temperature gradient associated with Gleeble tempering is covered in Appendix B. After samples were sectioned, as shown in Figure 3.7, the distance from the two lengthwise edges of the sectioned piece to the thermocouple position was measured, as illustrated in Figure 3.8. Five measurements were made from edges 1 and 2 to the location of the thermocouple (TC) for each Gleeble tempered Charpy specimen, per Figure 3.8. The five measurements from edge to TC location were
averaged to arrive at two length measurements per Gleeble tempering condition, or measurement from “edge 1” to TC and “edge 2” to TC. It should be noted that the labeling of the edges was arbitrary. These measurements were necessary, as mounting and polishing preparation for Vickers hardness indenting removed any indication of the original location of the thermocouple. While, theoretically, measurements from edge 1 to TC and edge 2 to TC should sum to the total length of the sectioned piece, variability in the alignment of the two percussion welds, indicating the location of the TC, introduced some inconsistencies. Additionally, measurements were made to the closest edge of the percussion weld; therefore, the diameter of the weld also factored in to the sum of the measurements, falling short of the total length of the sectioned piece. The two columns of indentations, as indicated in Figure 3.9, were positioned in accordance with the edge 1 and 2 measurements. Due to the slight inconsistencies mentioned in relation to TC weld positions and diameter, the distance between the two indentation columns in Figure 3.9 varied between 0.1 and 2 mm. Salt pot treated samples were sectioned transversely, such as A and B in Figure 3.3, and a 5 x 5 indentation matrix was used to determine the average hardness.

The hardness results are displayed in Figure 3.10, where the experimental tempering parameter, rather than the aim, is displayed on the x-axis. The aim tempering parameter is in reference to the tempering parameter, calculated with the times and temperatures in the time-temperature matrix of Table 3.2, while the experimental tempering parameter employs the tempering parameter calculated using the actual times and temperatures recorded during the heat treatment processes. The error bars displayed in Figure 3.10 are standard deviation of the sample. Only one sample per condition was tested for hardness, and the standard deviation displayed in Figure 3.10 correspond to the multiple (10) measurements taken per condition. The results shown in Figure 3.10 confirm that the time/temperature combinations calculated using the Hollomon-Jaffe tempering parameter produce nearly equivalent hardness values, as desired.

Figure 3.7 Cross-section position for all Gleeble® 3500 tempered specimens.
Figure 3.8 Illustration of measurements from lengthwise edges to thermocouple (TC) position.

Figure 3.9 Illustration of indentation positions for all Gleeble® 3500 tempered specimens. The distance between the two columns of indentations varied from 0.1 – 2 mm.

Figure 3.10 Rockwell C hardness (HRC) versus tempering parameter for each time-temperature combination where the (a) standard deviation of each measurement, overall trend line, and (b) associated times are displayed.
3.3.4 Charpy Blank Tempering

All 3600 s tempering was performed using salt pots at the Colorado School of Mines. Blanks were fully immersed in the appropriate salt medium for 1 hour and subsequently water quenched. No more than four blanks were tempered together at a time to prevent significant heat loss during initial submersion. Shorter tempers with times of 1, 10, and 100 s were achieved using the Gleeble® 3500. Heating rates ranging from ~600-1000 °C/s were achieved during Gleeble tempering of the Charpy blanks although programmed heating rates were set to approximately 1400 °C/s. The heating rate for salt pot treatments was assumed to be ~1 °C/s (based on time required to reach thermal equilibrium in liquid media according to ASTM E23 [66]). Further discussion related to heating rates is presented in Appendix C. Blanks were quenched in water from the tempering temperature for all salt pot treatments and quenched with helium gas in the Gleeble. Cooling rates of 30-60 °C/s were achieved during helium gas quenching. Stainless steel, full contact grips were used with a free span of 30 mm.

Times and temperatures of the tempering operations were recorded and used to calculate an equivalent isothermal tempering time for a target tempering temperature. This was achieved by converting the actual time-temperature profiles of the Gleeble tempering processes (heating and cooling included) to equivalent tempering parameters (see section 2.2.2 for isothermal tempering equivalence review). From these tempering parameters, equivalent tempering times could be extracted assuming a constant hold temperature at the tempering temperatures, as outlined in Table 3.2. All samples were processed with an aim equivalent tempering time of 1, 10, 100, or 3600 s. Figure 3.11 displays the equivalent tempering times calculated for the hour-long salt bath treatments. The equivalent tempering times for the 3600 s treatments range from approximately 3400 to 4200 seconds. Similar calculations were performed for the Gleeble® 3500 heat treated specimens with tempering times of 1, 10, and 100 s. The equivalent isothermal tempering times of each tempering operation are displayed in Figure 3.12. The temperature of the bath was monitored and used in the equivalent isothermal tempering calculations for all 3600 s tempers, while the temperature of each sample was monitored during Gleeble 3500 tempering.

To determine if the observed scatter in Figure 3.11 and Figure 3.12 for equivalent time is acceptable, tempering parameter was calculated using the experimental times and temperatures displayed in Figure 3.11 and Figure 3.12 and then compared to the corresponding aim tempering parameter. Figure 3.13 illustrates the results from these calculations. The maximum difference between the experimental and aim tempering parameters is approximately 60. Using the average experimental hardness for each tempering condition from Figure 3.10, one tempering parameter unit equates to approximately 0.003 HRC. This hardness to tempering parameter relationship was found by determining the average change in measured hardness with respect to tempering parameter, since the relationship is
nearly linear. The hardness and tensile strength differences associated with a tempering parameter difference of 60 were then calculated. Given one tempering parameter unit is approximately equivalent to 0.003 HRC, multiplying 60 by 0.003 gives a rounded hardness difference of 0.2 HRC. The conversion from hardness to tensile strength was made by comparing 4340 hardness-tensile data available in the literature [67]. Since the relationship between hardness and tensile strength is also nearly linear, a similar approach to determining the hardness to tempering parameter relationship was taken. One Rockwell C hardness unit was found to correlate to approximately 33 MPa for the reference 4340 steel. Given that a 60 TP difference is equivalent to a 0.2 HRC difference, the expected tensile strength difference is approximately 7 MPa (0.2 x 33). The steels in this study exhibit tensile strengths on the order of 1000 - 2000 MPa, rendering 7 MPa relatively insignificant. These calculations confirm that the scatter observed in Figure 3.11 and Figure 3.12 is acceptable. The tempered blanks were therefore determined to be fit for further machining and subsequent mechanical testing.

Figure 3.11  Equivalent tempering time versus tempering temperature for Charpy blanks. The dotted lines signify the desired equivalent tempering time. Each data point represents a batch of 1 – 4 Charpy blanks.
Charpy Specimen Preparation

Following hardening and tempering in the blank form, Charpy specimens were machined following the ASTM standard, as illustrated in Figure 3.14 [66]. All specimens were machined in the longitudinal-transverse orientation, as depicted in Figure 3.16. The position of the notch with respect to the Charpy blank is particularly crucial for the blanks tempered in the Gleeble, due to the gradient in 

![Figure 3.12](image1.png)

Figure 3.12 Equivalent tempering time versus tempering temperature for Gleeble Charpy blanks. The dotted lines signify the desired equivalent tempering time. Each data point represents 1 Charpy blank.

![Figure 3.13](image2.png)

Figure 3.13 Experimental tempering parameter versus aim tempering parameter for Charpy blanks and all tempering times.

3.3.5 Charpy Specimen Preparation

Following hardening and tempering in the blank form, Charpy specimens were machined following the ASTM standard, as illustrated in Figure 3.14 [66]. All specimens were machined in the longitudinal-transverse orientation, as depicted in Figure 3.16. The position of the notch with respect to the Charpy blank is particularly crucial for the blanks tempered in the Gleeble, due to the gradient in
temperature along the length of the specimen. For this reason, the notch was machined at the point at which the desired degree of tempering was achieved. This point on the sample corresponds with the position of the thermocouple, at approximately the mid-length of the blank. All notches were machined via wire fed electrical discharge machining (EDM). To ensure the removal of any Charpy blank surface effects, material was removed uniformly from all sides during machining.

Figure 3.14  Drawing of Charpy specimen. All dimension and tolerances in mm.

Figure 3.15  Illustration of Charpy orientation with respect to original plate. Not to scale.

3.4 Material Processing – Part II: Tensile Specimens

Tensile blanks were also machined from the as-received plate material and then quenched and tempered. As with the Charpy specimens, conventional tempering (3600 s) was performed in salt baths, while short-time tempering (1-100 s) was performed using the Gleeble 3500. After heat treating, the tensile blanks were machined to their final tensile specimen geometry. Supplemental information concerning the characterization of the thermal gradient and design process of the final tensile geometry can be found in Appendices B and D.
3.4.1 Tensile Blank Geometry

Tensile blanks, with the geometry outlined in Figure 3.16, were machined from the original plate material for hardening and tempering. All tensile blanks were machined longitudinally with respect to the original plate rolling direction and centered with respect to plate thickness, as depicted in Figure 3.17. The length was designed to include a 100 mm free span, as well as 30 mm on each side for gripping in the Gleeble. A 2 mm through-hole was added to the blank to allow for simplified salt pot hardening and tempering. For specimens tempered in the Gleeble, 10 mm, including the through-hole, was removed from one end prior to tempering to arrive at a specimen length of 160 mm. Specifics as to why these tensile blank dimensions were chosen are further discussed in Appendix B and Appendix D.

![Figure 3.16 Drawing of tensile specimen. All dimension and tolerances in mm. Not to scale.](image)

![Figure 3.17 Illustration of tensile specimen orientation with respect to original plate. Not to scale.](image)

3.4.2 Tensile Blank Austenitizing and Tempering

The tensile blanks were austenitized at 845 °C for 1 hour and quenched to room temperature in agitated oil. Tensile blanks were austenitized and quenched at the Colorado School of Mines with available salt pots. No more than four blanks were austenitized together at a time to prevent significant heat loss during immersion. The temperature of the quench oil was monitored and cooled, so as not to exceed 30 °C. The same process to confirm through-hardening of the Charpy blanks was also performed.
for the tensile blanks, where the hardness of an as-quenched sample was measured and compared to the expected hardness of a fully martensitic microstructure. Following the same criteria used to determine if the Charpy blanks were fully hardened, the tensile blanks were also considered to have undergone full hardening confirmed by hardness testing.

Tensile blank tempering was performed to be consistent with the process outlined in section 3.3.4 for Charpy blank tempering. The heating rates achieved in the Gleeble remained relatively consistent (~600 °C/s) for tensile blank tempering and the free span utilized in Gleeble tempering of the tensile blanks was 100 mm. The heating rate for all salt pot treatments was assumed to be ~1 °C/s.

Figure 3.18 displays the equivalent tempering times calculated for the hour long salt bath treatments. The equivalent tempering times for the 3600 s treatments ranged from approximately 3300 to 4300 seconds. Similar calculations were performed for the Gleeble® 3500 heat treated specimens with tempering times of 1, 10, and 100 seconds. The equivalent isothermal tempering times of each tempering operation are displayed in Figure 3.19.

Figure 3.18 Equivalent tempering time versus tempering temperature for tensile blanks. The dotted lines signify the desired equivalent tempering time. Each data point represents a batch of 3-4 tensile blanks.
The tempering parameter was calculated using the actual times and temperatures (heating and cooling included) for each treatment and compared to the corresponding aim tempering parameter, as displayed in Figure 3.13. In section 3.3.4, 60 TP units was suggested to be an acceptable deviation from the aim tempering parameter; therefore, all tensile blank tempering operations were checked to ensure that a deviation of 60 TP was not exceeded. If the tempering parameter deviation exceeded ±60, then the sample was not approved for testing and the tempering treatment was repeated with a different sample.

Figure 3.19 Equivalent tempering time versus tempering temperature for Gleeble tensile blanks. The dotted lines signify the desired equivalent tempering time. Each data point represents 1 tensile blank.

The tempering parameter was calculated using the actual times and temperatures (heating and cooling included) for each treatment and compared to the corresponding aim tempering parameter, as displayed in Figure 3.13. In section 3.3.4, 60 TP units was suggested to be an acceptable deviation from the aim tempering parameter; therefore, all tensile blank tempering operations were checked to ensure that a deviation of 60 TP was not exceeded. If the tempering parameter deviation exceeded ±60, then the sample was not approved for testing and the tempering treatment was repeated with a different sample.

Figure 3.20 Experimental tempering parameter versus aim tempering parameter for tensile blanks and all tempering times.
3.4.3 Final Tensile Geometry

The final tensile specimen geometries for all short-time and conventional conditions are displayed in Figure 3.21 and Figure 3.22, respectively. The short-time tempered tensile specimens feature a 60 mm reduced cross-section length, while all conventional specimens have a reduced cross-section length of 20 mm. This difference resulted from a machining error, and additional information on the development of the final tensile specimen geometries is located in Appendices B and D. Tensile specimens were originally designed in accordance with Figure 3.22 to ensure fracture would occur within the 10 mm extensometer gauge length. Due to the machining error associated with the short-time tempers and the resultant increase in the specimen gage length as depicted in Figure 3.21, the likelihood of fracture occurring within the 10 mm extensometer gauge length was reduced. In order to assess any possible effects from differences in tensile geometry between the short and conventional time conditions, two specimens per temperature condition were machined according to Figure 3.22 for the 1 s conditions.

![Figure 3.21](image1)

Figure 3.21 Final tensile specimen geometry for all short-time (1, 10, 100 s) tempers. Specimens were tested using a 10 mm extensometer. Not to scale. All dimensions in mm.

![Figure 3.22](image2)

Figure 3.22 Final tensile specimen geometry for conventional tempers of 3600 s. Additional two specimens per temperature condition were machined according to this geometry for the 1 s time conditions to assess any possible tensile property differences associated with difference in geometry. Specimens were tested using a 10 mm extensometer. Not to scale. All dimensions in mm.
3.5 Material Processing – Summary

Figure 3.23 summarizes the material processing procedures detailed in the previous sections. Table 3.3 displays specific hardness, heating rate, and tempering parameter information for the various time-temperature combinations. Charpy and tensile blanks were machined from as-received 12.7 mm (0.5”) plates. Blanks were conventionally austenitized in a vacuum furnace or salt pot and then oil quenched. Following confirmation via hardness measurements that blanks were through-hardened, blanks were tempered using the Gleeble and salt pots. Short-time tempers (1, 10, 100 s) were conducted in the Gleeble, while conventional (3600 s) tempers were performed in salt pots. Tempered Charpy and tensile blanks were final machined for subsequent mechanical testing. Additional information on parameters such as thermal gradient, thermal overshoot, and tempering time adjustments considered during Gleeble tempering is located in Appendices B, C, E, F, and G.

Figure 3.23 Illustration of material processing of Charpy, tensile, XRD, and hardness specimens, all dimensions in mm unless otherwise specified. * Coupons were taken from specific locations within tempered Charpy and tensile blanks. Hardness and XRD coupon locations with respect to blanks are presented in sections 3.3.3 and 3.7, respectively.
### Table 3.3 Material Processing Summary

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Temperature (°C)</th>
<th>Approximate TP</th>
<th>Average Hardness from Test Matrix (HRC)</th>
<th>Approximate Charpy Heating Rate (°C/s)</th>
<th>Approximate Tensile Heating Rate (°C/s)</th>
<th>Tempering Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>305</td>
<td>9250</td>
<td>57.9</td>
<td>870</td>
<td>600 - 650</td>
<td>Gleeble</td>
</tr>
<tr>
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<td>271</td>
<td>10200</td>
<td>57.8</td>
<td>850</td>
<td>600 - 650</td>
<td>Gleeble</td>
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<td></td>
<td>56.6</td>
<td>760</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>200</td>
<td></td>
<td>58.1</td>
<td>1</td>
<td>1</td>
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<td>11200</td>
<td>54.4</td>
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<td>600 - 650</td>
<td>Gleeble</td>
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<td>13150</td>
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<td>47.1</td>
<td>650**</td>
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<td></td>
</tr>
<tr>
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<td></td>
<td>48.4</td>
<td>1</td>
<td>1</td>
<td>Salt Pot</td>
</tr>
</tbody>
</table>

*Mistake during test matrix heat treating led to no sample being available for this condition to monitor hardness. Using an additional sample was not considered at the time as all other hardness values confirmed the validity of the time-temperature matrix. Additionally, it was of interest to conserve samples for Charpy testing purposes.

**Specimens for heating rate study; additional information is located in Appendix C

### 3.6 Mechanical Testing

The experimental methods related to Charpy, tensile, and Vickers microhardness testing are reviewed in this section.
3.6.1 Charpy Testing

Charpy testing was conducted in accordance with ASTM E23 [66], with the exception of high temperature testing, as will be discussed. Specimens were tested at approximate temperatures of -200, -100, 0, 25, 100, and 200 °C. Liquid nitrogen was used for testing temperatures of approximately -200 °C, while a mixture of liquid nitrogen and ethanol was used to achieve temperatures near -100 °C. Iced water and oil were utilized for testing temperatures of 0 and 100 °C, respectively. A furnace, along with a surrounding thermal mass, was used to achieve testing temperatures of 200 °C. Two samples per tempering condition were tested for the room temperature tests.

ASTM E23 [66] dictates that, if using a gas medium to heat the sample (e.g. air), the specimen must be immersed for at least 30 minutes prior to testing to ensure through-heating of the sample. However, due to the short-time, low-temperature heat treatments utilized in this study, additional tempering of the material is of concern when heated to 200 °C and held over 30 minutes. Per the standard, liquid media only require 5 minutes of immersion time prior to testing; however, oil and salt liquids were not utilized at 200 °C here due to safety complications associated with off-gas, smoke, and the necessary use of a fume-hood. Therefore, a furnace with the added component of a surrounding thermal mass was used. Aluminum was chosen for the thermal mass material due to its availability and high thermal conductivity. To determine the minimum time required to reach the desired temperature, thermal tests were performed. Figure 3.24 illustrates the thermal mass configuration used for the 200 °C Charpy tests. The aluminum and steel masses were heated using a furnace and were allowed to reach temperature over many hours. The masses remained within the furnace during the thermal testing outlined here. A thermocouple was placed between the steel block and aluminum base plate, as well as within the sample. The sample thermocouple was inserted into a hole drilled through the center of the sample, as illustrated in Figure 3.24. Once the specimen was placed into the slot, the block and specimen thermocouples were monitored and recorded every minute for 15 minutes. As displayed in Figure 3.25, the specimen temperature matched the block temperature most closely after 5 minutes of heating. Therefore, 5 minutes was chosen for the appropriate equilibrium time for the 200 °C tests. The preliminary tests were repeated 7 times, with 10 minutes between each test to allow for the thermal mass to re-equilibrate. Therefore, 10 minutes was scheduled between each heating cycle during actual testing and no more than 7 specimens were tested consecutively. Following the testing of the 7th specimen, the thermal mass was allowed at least 1.5 hours in the at-temperature furnace to re-equilibrate.
Charpy data, for both toughness and pct. shear lip, were fit using the hyperbolic tangent function \[68\]:

\[
Y = A + B \cdot \tanh \left( \frac{T - T_o}{C} \right)
\]  

(3.1)

where A is the energy midpoint, B is the toughness range from midpoint A to the upper and lower energy shelves, T_o is the mid transition temperature, and C is the temperature range from midpoint T_o to the upper and lower energy shelves with respect to temperature. The physical interpretation of the coefficients A, B, T_o, and C are illustrated in Figure 3.26. The upper and lower shelves are represented by A+B and A-B, respectively. The slope of the linear region is expressed as B/C. Fits were determined with a least squares regression analysis, in conjunction with Equation 3.1.
Equation 3.1 was used to fit the majority of the Charpy results, including both the energy and percent (%) shear data; however, certain conditions did not produce a classic sigmodal relationship associated with ductile-to-brittle transition temperature (DBTT) Charpy data when utilizing Equation 3.1, and for other conditions a different curve shape was thought to better fit the results. For these conditions, curves were drawn manually to more accurately represent the data. These curves are identified throughout the text by dashed lines and are identified in corresponding figure captions. Figure 3.27 illustrates the fit produced using Equation 3.1, compared to the manual fit method for two conditions: 300 and 400 °C tempers at 1 h percent (%) shear and impact energy, respectively.

The temperature correlating to 15 ft-lbs (\(C_v, 15\)) of energy was chosen as one of the means to quantitatively compare the DBTT Charpy results. This index was chosen due to the difficulty of establishing a distinct upper and lower shelf energy for some conditions. Characterizing the fracture surfaces also proved to be challenging for some conditions studied; therefore, fracture appearance transition temperature (FATT) was not used. The 15 ft-lb index, \(C_v, 15\), was obtained by determining the temperature at which each DBTT curve intersected 15 ft-lbs of energy. All \(C_v, 15\) values obtained from manual fit curves are denoted by open data points and are called out in corresponding figure captions.
3.6.2 Tensile Testing

Uniaxial tensile testing was carried out on an MTS 22-kip hydraulic frame equipped with vee-wedge grips. Displacement was measured using a 10 mm extensometer with a strain rate of 0.015 mm/mm/min. If the extensometer reached its limit of 15 %, then the program was stopped and the extensometer reset. Extensometer resets are apparent in many of the stress-strain curves via a jog in the stress-strain data. Prior to testing, five diameter measurements were taken along the reduced cross-section within the specified extensometer range. The five measurements were averaged for engineering stress calculations, while the change in gage length given by the extensometer was used for engineering strain calculations. Ultimate tensile strength (UTS) was taken to be the highest stress value. Yield strength (YS) was calculated using the 0.2 % offset method [69].

Sample standard deviation of all tensile property parameters was calculated utilizing the appropriate number of tested specimens per time-temperature combination, as indicated in Appendix H.
One to five samples were tested per condition, with the specific number of samples per condition outlined in Appendix H. The number of samples per condition varied due to complications in the gripping process. High hardness in the gripping section and high tensile strengths resulted in slipping within the grips. To minimize damage to the grips while testing as many conditions as possible, lower strength specimens were tested first. After completion of the lower strength conditions (11,000, 12,000, and 13,000 TP), one sample per time-temperature combination at higher strength tempering parameters (9,000 and 10,000 TP) was tested. This process, of cycling through one specimen per high strength time-temperature condition, was continued until the first indication of substantial slipping was observed. Testing was terminated at this point in order to preserve the grips for further use (on other projects).

Reduction of area (RA) measurements were made following tensile testing. The smallest, complete diameter of the fractured specimen was measured five times to arrive at an average $d_f$ for each condition. Reduction of area was calculated using the equation:

$$RA = \frac{A_o - A_f}{A_o} \times 100$$  \hspace{1cm} (3.2)

where $A_o$ and $A_f$ are the initial and final cross-sectional areas, respectively.

### 3.6.3 Vickers Microhardness

Samples were prepared via mounting and polishing to a 6 µm finish. Microhardness measurements were conducted using a LECO MHT200 microhardness indenter. A 500 g-f load and 10 s dwell time were used to determine Vickers hardness. Rockwell C (HRC) values reported were obtained using the conversion capabilities of the LECO microhardness indenter.

### 3.7 X-Ray Diffraction

X-ray diffraction (XRD) samples were prepared by sectioning the tempered tensile blanks, as indicated in Figure 3.28, and lightly grinding the appropriate face with a progression of 250, 320, 400, and 600 grit sand paper. Samples were subsequently thinned in a solution of 10 parts deionized water, 10 parts hydrogen peroxide, and 1 part hydrofluoric acid for 15 to 30 minutes, to achieve a thickness reduction of at least 0.005 in. as per ASTM standard E975 [70].

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Retained austenite volume fractions were determined using nickel-filtered copper radiation and a Phillips X-pert diffractometer with operating conditions of 40 kV and 40 mA. The diffractometer was instrumented with an X’celerator detector and 1° slit. Four ferrite/martensite peaks ({110}, {200}, {211}, {220}) and four austenite peaks ({111}, {200}, {220}, {311}) were compared to determine the amount of retained austenite. Samples were scanned over a 2θ range of 40 to 105°, with a step size of 0.05° and 200 s dwell time. Each sample, for a unique condition, was run four times in an attempt to decrease uncertainty. Two measurements were conducted at the same orientation, and then the sample was rotated 90° and measured two more times.

Peaks were fit utilizing the peak fitting software available through PANalytical HighScore. The Cu K-α2 wavelength was removed from the spectra to simplify later analyses. Peak fitting was then performed with “Profit” available in HighScore. The full-width-half-max and height of the identified peaks were used to determine the experimental intensity of each peak. Retained austenite percentages were calculated in accordance with the SAE method [71] using the equation

$$V_γ = \frac{1/n_γ \sum^n \frac{i^{hkl}}{R^{hkl}_γ}}{1/n_γ \sum^n \frac{i^{hkl}}{R^{hkl}_γ} + 1/n_α \sum^n \frac{i^{hkl}}{R^{hkl}_α}}$$  \hspace{1cm} (3.3)$$

where \(V\) is the volume fraction, \(n\) is the number of peaks associated with the phase in question, \(I\) is the intensity, and \(R\) is the theoretical intensity.
3.8  Fractography

Charpy fracture surfaces were examined macroscopically using a Nikon D70 camera equipped with a macro lens and reversing ring. An ISO setting of 10 and a 16 f-stop were utilized for all images. Charpy fracture surfaces were further examined for brittle point fraction analysis using a JEOL 7000 FESEM operated at 20 KeV accelerating voltage and a 10 mm working distance. Micrographs were taken at consistent positions within the examined specimens, as illustrated in Figure 3.29.

![Figure 3.29 Illustration of FESEM micrograph positions used for brittle point fraction evaluation.](image)

3.8.1  Percent Shear Lip

While Charpy fracture surfaces are often evaluated in terms of pct. ductile and pct. brittle area, the fine structure of tempered martensite somewhat limits this characterization. Typically, brittle regions are easily identified by their shiny appearance, due to large cleavage facets that reflect light. However, shiny features were not identifiable on the fracture surfaces in this study, even for extremely brittle cases. Therefore, the percentage of the fracture surface exhibiting shear lips was used, in conjunction with absorbed energy data, to compare conditions.

An image processing program, ImageJ, was used to evaluate the fracture surfaces. Following macro imaging of the surfaces, the images were evaluated by outlining the shear lip regions, as displayed in Figure 3.30. After outlining, the threshold was adjusted to display the outlined regions as black and the remaining areas as white. The area of the original Charpy fracture surface was then evaluated with the particle analyzer feature in ImageJ. This analysis provided an area percentage that was then taken as the percentage of the fracture surface that contained shear lip features. An example of the product of the particle analyzer with the shear lip percentage is displayed in Table 3.4.
After outlining, the threshold was adjusted to display the outlined regions as black and the remaining areas as white. The area of the original Charpy fracture surface was then evaluated with the particle analyzer feature in ImageJ. This analysis provided an area percentage that was then taken as the percentage of the fracture surface that contained shear lip features. An example of the product of the particle analyzer with the shear lip percentage is displayed in Table 3.4.

Table 3.4  Corresponding Shear Lip Area for Figure 3.30.

<table>
<thead>
<tr>
<th>Sample</th>
<th>%Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>100-404-RT</td>
<td>19.1</td>
</tr>
</tbody>
</table>

3.8.2  Brittle Point Fraction

Using a field emission scanning electron microscope, 2-D projections of the Charpy fracture surfaces were obtained and used to quantify the brittle point fraction for various conditions. The brittle point fraction is defined here as the number of brittle cleavage fracture points divided by the total number of points, where points were counted at the intersection of lines on a grid, much like the point counting method used for determining phase volume fraction. There are several scenarios outlined in ASTM standard E562 [72] to assist in determining the number of images that must be analyzed, with varying levels of associated relative accuracy. Thirty-three pct. relative accuracy is the lowest passable relative accuracy presented in the E562 standard and was chosen as the threshold for this study to reduce the number of fields required to reach an acceptable accuracy. Relative accuracy is defined as [72]:

![Illustrative example of outlining process for evaluation of % shear lip, including (a) original image of fracture surface, (b) filled in shear lip area image, and (c) resultant outlined area evaluated by the particle analyzer feature in ImageJ.](image-url)
The grid size was chosen by consulting Table 3.5, taken from ASTM standard E562. A 100-point grid was selected to evaluate each condition to decrease the number of fields needed to achieve 33 pct. relative accuracy, where only 4 fields are estimated to be necessary for phases occupying 10-20 volume percent. Point spacing was approximately 20 microns. Four fields were evaluated initially, and if the relative accuracy of the 4 fields was at least 33 pct., then no additional fields were examined. However, in one instance the desired relative accuracy was not achieved, and three additional fractographs were examined. Actual overlaid grids contained either 108 or 99 points, due to the fractograph dimensions. The grid was offset randomly for each measurement.

Table 3.5  Area Fraction and Field Number Reference [72]

<table>
<thead>
<tr>
<th>Area Fraction, in Percent</th>
<th>33% Relative Accuracy</th>
<th>Number of fields n for a grid of</th>
</tr>
</thead>
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<td></td>
<td>16 points</td>
<td>25 points</td>
</tr>
<tr>
<td>2</td>
<td>110</td>
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<tr>
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</tr>
<tr>
<td>20</td>
<td>15</td>
<td>10</td>
</tr>
</tbody>
</table>

Since 3-D features were not taken into account during the quantification of the fractographs, the measurements are not referred to as “percent brittle” or “percent ductile”, as this may be misleading. Fracture surfaces were quantified in order to compare the fracture behavior of the various conditions; consequently, the lack of 3-D consideration is considered acceptable for the purposes of this study.

For the quantitative point count, brittle and ductile fracture points were defined by the following criteria. Microvoid coalescence and features that appeared to exhibit plastic deformation were counted as ductile fracture points. Flat facets, with no evidence of ductile tearing, were counted as brittle fracture. Transition regions were tallied as a third entity, then split between ductile and brittle fracture after point counting of the fractograph was complete. A point was counted as a transition region if the cross-section fell at the intersection of a ductile and brittle region, or if the region was unidentifiable as either ductile or brittle. Figure 3.31 illustrates an example showing points that would be considered brittle (Figure 3.31 point A) and ductile (Figure 3.31 point B). It should be noted that the magnification of this micrograph is higher than the magnification used for the actual point counts, and is only utilized for illustration purposes.
Figure 3.31 Illustrative example of points considered to be (A) brittle and (B) ductile.
CHAPTER 4
RESULTS AND DISCUSSION

This chapter presents Charpy V-notch impact toughness, x-ray diffraction, tensile, and fractography results pertaining to the conventionally and short-time tempered specimens. Specifically, results relating to Charpy impact energy at room temperature, ductile to brittle transition temperature, retained austenite content, ultimate tensile strength, yield strength, and reduction of area are presented and discussed. Analysis of time-temperature equivalence with respect to the Hollomon-Jaffe tempering parameter and characteristic diffusion distance is also presented.

4.1 Retained Austenite

Figure 4.1 displays retained austenite content as a function of tempering parameter for each time condition. As tempering parameter increases, there is a corresponding decrease in retained austenite content. For all conditions, the most substantial decrease in retained austenite is observed between 10,000 and 11,000 TP. A difference between tempering time conditions is observed, where austenite decomposition is retarded with shorter tempering times, resulting in a higher retained austenite content with decreasing tempering time for a given tempering parameter.

![Figure 4.1 Retained austenite (vol %) as a function of tempering parameter for all time conditions, where each data point is an average of 4 values. Displayed (a) without and (b) with standard deviation error bars.](image)

While retained austenite results in Figure 4.1 are fairly systematic with respect to tempering time, it is important to recognize the limitations associated with measuring low percentages of retained austenite using XRD. There have been varying reports on the minimum amount of retained austenite
reliably detected by XRD, ranging from ~1.5 to 2 % [70, 73]. Additionally, the calculated amount of retained austenite at small percentages can be significantly affected by peak fitting operations. Four measurements were made per condition to assess the variability in the measurements. Standard deviation for each measurement is included in Figure 4.1b. As seen here, the standard deviation of the measurements went from low values up to approximately 3.5% retained austenite. It may be of interest to explore more accurate techniques for measuring small amounts of retained austenite in the future. For the purposes of this study, the retained austenite results will be utilized to relate microstructure and properties, as these data are the primary source of information related to microstructure; however, the limitations of these results should be noted and considered.

Retained austenite values associated with the 3600 s condition are compared with existing literature [16] for 4340 steel in Figure 4.2, where the two data sets are shown to correlate well. Figure 4.3 is taken from the same study by Williamson et al. [16], and also displays fraction of cementite with respect to tempering temperature. The retained austenite and cementite volume fractions in Williamson et al. [16] were measured using Mossbauer spectroscopy. As retained austenite diminishes, the fraction of cementite is shown to increase, a process often associated with the second stage of tempering and TME. The reduced amount of retained austenite decomposition with shorter tempering times (at a given TP) observed in Figure 4.1 may therefore be of interest with respect to its potential relationship with cementite formation. As portrayed in Figure 4.1, retained austenite decomposition is slowed with shorter tempering times at an equivalent TP, presenting the possibility of a corresponding retardation in cementite formation and growth. While there is some indication from the present retained austenite results that there may be an effect on cementite formation and growth, further investigation involving direct examination of cementite is needed to make definitive conclusions on the effect of short-time tempering on cementite nucleation and growth behavior.

In addition to possible effects on cementite nucleation and growth, the difference in retained austenite decomposition behavior between tempering time conditions within the same tempering parameter regime suggests a dissimilarity in kinetics, where shorter tempering times exhibit a slower kinetic response. The kinetic differences implied at an equivalent tempering parameter are noteworthy, as the tempering parameter is employed to achieve an equivalent degree of tempering. However, as seen here, it seems that equivalent hardness (tempering parameter) is not a complete indicator for equivalent kinetic response (with respect to austenite decomposition) during tempering. The concept of kinetic differences at an equivalent tempering parameter is further discussed in section 4.5, where mechanical property results are also considered.
This section discusses the results of Charpy V-notch impact testing related to room temperature testing and ductile to brittle transition temperature testing.

Figure 4.2 Retained austenite (vol %) as a function of tempering temperature comparing 3600 s condition results to the literature [16].

Figure 4.3 Fraction of retained austenite and cementite versus tempering temperature for 4340 and 4130 steel. Tempering temperatures are associated with a tempering time of 1 hr. Adapted from [16].

4.2 Charpy V-Notch (CVN) Testing

This section discusses the results of Charpy V-notch impact testing related to room temperature testing and ductile to brittle transition temperature testing.
4.2.1 Charpy Energy at Room Temperature

Room temperature Charpy V-notch (CVN) impact toughness was determined for each time condition and is displayed with respect to tempering parameter in Figure 4.4 and summarized in Figure 4.5. From the as-quenched condition to a tempering parameter of approximately 9,000 (200 °C for 1 hr), CVN absorbed energy increases for all conditions. The observed increase in impact energy from the as-quenched condition to ~9,000 TP is similar for all tempering time conditions; however, at a tempering parameter of approximately 10,000 (250 °C for 1 hr), toughness behavior between the various time conditions begins to diverge.

For a tempering time of 3600 s, room temperature impact energy follows the expected trend associated with TME, where a toughness trough is observed between 9,000 and 13,000 TP. As tempering time decreases within an equivalent tempering parameter regime, there is a systematic increase in toughness and a flattening of the toughness trough (representing TME), as portrayed in Figure 4.5. This result is important, indicating that short-time tempering diminishes tempered martensite embrittlement.

Figure 4.4 Energy absorbed at room temperature as a function of tempering parameter for (a) 3600 s, (b) 100 s, (c) 10 s, and (d) 1 s. Two samples were tested for each condition; a single point for any one condition implies that the two samples yielded identical results.
Hardness values between tempering conditions were shown to be similar for a given tempering parameter in section 3.3.3 (Figure 3.10), with the largest difference in hardness being 2.2 HRC between the 10 and 3600 s conditions at a TP of 13,000. It is helpful to confirm the differences in impact energy displayed in Figure 4.4 and summarized in Figure 4.5 are not the result of slight variations in hardness between tempering conditions. Figure 4.6 displays Charpy V-notch impact energy as a function of hardness, where hardness is represented on a decreasing axis. The overall trends associated with impact energy in relation to hardness are consistent with trends displayed in Figure 4.5, where impact energy increases with decreasing tempering time at an equivalent hardness level (tempering parameter) and the TME trough is diminished. The results displayed in Figure 4.6 confirm CVN impact energy trends are not the product of a slight difference in hardness values between tempering conditions at a given tempering parameter, and reinforce the conclusion that short times at elevated temperature diminish TME.

Tempered martensite embrittlement has been attributed to several mechanisms within the literature, each differing only subtly. The embrittlement phenomenon is often attributed to the decomposition of interlath austenite to thin cementite films [2, 3, 27, 74–76], where these films then act as preferred crack initiation and propagation sites. The greater austenite fractions obtained at short times (for a given TP) offer a potential explanation for the reduced TME behavior. While the decomposition of austenite and the formation of cementite are often claimed to be the mechanisms responsible for TME, others argue that the subsequent coarsening of cementite is the true cause of TME [5, 6, 77]. While these prominent theories differ slightly, cementite plays a central role in both mechanisms.
Due to the frequent connection of TME to the decomposition of retained austenite during tempering, the impact toughness behavior presented here is significant in the context of retained austenite decomposition behavior that was presented in the previous section (4.1). As tempering time is decreased within an equivalent tempering parameter regime, retained austenite decomposition and TME have been shown to simultaneously diminish. As the connection between TME and retained austenite decomposition is typically associated with the decomposition of retained austenite to interlath cementite, it is likely that retained austenite decomposition behavior exhibited in section 4.1 has a significant effect on cementite nucleation and growth in a manner that serves to diminish TME. While retained austenite content and toughness results suggest that short-time tempering has an effect on cementite nucleation and growth, it is difficult to speculate on the nature of the effects on cementite behavior without additional microstructural information. Microstructural information pertaining to the change of cementite size, morphology, and distribution with tempering time at an equivalent tempering parameter would help to enlighten the microstructural mechanisms responsible for the improved toughness properties with short-time tempering exhibited in Figure 4.5.

In addition to the possible effects of cementite nucleation and growth, the potential role of transition carbides on toughness behavior is acknowledged. Transition carbides have been shown to form during oil quenching of 4340 steel [78]. Upon subsequent tempering, transition carbides may coarsen and eventually be replaced by cementite and ferrite during the third stage of tempering. It is probable that transition carbides are present after quenching and tempering for the time-temperature combinations

Figure 4.6  Energy absorbed at room temperature as a function of hardness for all conditions. Two samples were tested for each condition; a single point for any one condition implies that the two samples yielded identical results.
explored here; therefore, the coarsening behavior of these carbides may have a marked effect on the toughness behavior observed in Figure 4.5. Future investigations involving cementite and transition carbide type, size, spacing, and morphology characterization may help to reveal the role of these carbides in contributing to the toughness behavior observed here.

Differences between the present TME trough behavior and other techniques within the literature employed to avoid TME should be noted. Higher silicon containing steels (such as 300-M) have been shown to delay the manifestation of TME to higher tempering temperatures (at a constant tempering time) via the retardation of cementite formation [3], exhibiting a shifting of the TME trough to higher tempering temperatures or tempering parameters. It should be noted that the current results do not exhibit this behavior. In Figure 4.5, the TME impact energy trough does not shift with shorter tempering times, but rather diminishes in magnitude with decreasing tempering time and remains within the same tempering parameter regime. The differences in the details of TME “improvement” due to rapid tempering in comparison to Si-aided 300-M are not currently understood. More detailed characterization of microstructure evolution during tempering may help clarify the origin of these differences.

4.2.2 Charpy Energy Transition Curves

Charpy impact testing was also conducted at a variety of testing temperatures in order to characterize the ductile to brittle transition temperature behavior for the various tempering conditions. Figure 4.7 displays a comparison of the obtained DBTT curves for the various tempering times at equivalent tempering parameters. Brittle and ductile point fractions used to inform manual fitting (dashed lines) are presented in Appendix I and curves including data points are located in Appendix J. The corresponding tempering parameter associated with each set of curves is denoted at the top left of Figure 4.7a through Figure 4.7d. The specific tempering temperatures for each tempering condition can be found in Table 3.2.

At a tempering parameter of ~9,000 (Figure 4.7a), there is little distinguishable difference between the DBTT curves for each time condition. As tempering parameter increases, the DBTT curves of the various time conditions exhibit differences. The separation of the curves reveals a shift in transition temperature to lower temperatures with decreasing tempering time at an equivalent tempering parameter. In addition to this lateral shift, there is an observed increase in high (testing) temperature energy with decreasing tempering time at a constant tempering parameter. Upper shelf energy was not quantified in this study as many of the DBTT curves in Figure 4.7 do not exhibit a clear upper shelf for the testing temperatures employed. Despite the lack of upper shelf energy quantification, it is apparent from Figure 4.7 that impact energy systematically increases with shorter tempering times at high (200 °C) testing temperatures and that many of the DBTT curves are approaching the upper shelf energy at 200 °C
testing temperature. This behavior suggests an increase in upper shelf energy with decreasing tempering time at an equivalent tempering parameter. Upper shelf energy depends on the formation and growth of voids. The formation and growth of voids depends on many factors including: second-phase particle size and shape, stress state, matrix strength, particle-matrix cohesion, impurity atom concentration at particle-matrix interfaces, strain rate, and strain hardening rate [1, 33, 34, 48, 79, 80].

The DBTT index temperature, $C_{\nu} 15$, is compared to better quantify the changes in the DBTT behavior with tempering time. Figure 4.8 displays $C_{\nu} 15$ with respect to tempering parameter for the four tempering time conditions. The 3600 s condition exhibits an initial increase in $C_{\nu} 15$ with tempering parameter. At ~11,000 TP (300 °C for 1 hr), $C_{\nu} 15$ reaches a maximum and then begins to decrease with tempering parameter. Besides a decrease in room temperature impact energy, TME is recognized as an increase in transition temperature; therefore, the peak in transition temperature associated with the 3600 s condition is an indication of TME. As tempering time is decreased within the same tempering parameter regime, there is an observed leveling out of the transition temperature peak (diminishing of TME), where $C_{\nu} 15$ – tempering parameter trends become more linear. Furthermore, the $C_{\nu} 15$ values are shown to
decrease overall with decreasing tempering time at an equivalent tempering parameter, indicating an overall improvement in toughness along with TME diminishment. In summary, the toughness behavior observed at room temperature (Figure 4.5), where shorter tempering times were shown to diminish TME via an increase in toughness, is also reflected in the transition temperature results presented in Figure 4.7 and Figure 4.8.

4.2.3 Fracture Appearance of CVN (Shear Lips)

To support the Charpy DBTT findings presented in section 4.2.2, Charpy fracture surfaces were examined to determine pct. shear lip fracture. This type of analysis offers confirmation of the impact energy data, as well as some insight into the fracture behavior of the various conditions. Results are displayed in Figure 4.9, where the various time conditions are compared at equivalent tempering parameters. Fracture surface images used to determine pct. shear lip are presented in Appendix K and pct. shear lip curves, including data, are located in Appendix L. As shown in Figure 4.9, there is not a significant difference between time conditions at lower tempering parameters of 9,000 and 10,000. At 11,000 TP, the curves begin to diverge and continue to become more distinct with increasing tempering parameter. With a decrease in tempering time at an equivalent tempering parameter, the pct. shear lip transition curves are observed to shift to lower testing temperatures, indicating a greater degree of shear fracture at lower testing temperatures. Figure 4.10 shows the fracture surfaces of two tempering conditions (1 and 3600 s at 13,000 TP) tested at room temperature and -100 °C. Figure 4.10 depicts what
was quantitatively introduced in Figure 4.9, where it is apparent that the shorter tempering time condition exhibits a larger area percentage of shear lips.

![Figure 4.9 Percent shear lip as a function of testing temperature for tempering parameters of (a) 9,000, (b) 10,000, (c) 11,000, (d) 12,000 and (e) 13,000 for times of 3600, 100, 10, and 1 s. Dotted lines denote hand fit curves.](image_url)

The pct. shear lip results presented here are consistent with the DBTT trends in section 4.2.2. Decreasing tempering time at an equivalent tempering parameter produces a decrease in transition temperature as well as an increase in pct. shear lip at lower testing temperatures. As ductile (shear) fracture is known to increase the energy required for fracture, the decrease in transition temperature and simultaneous increase in pct. shear lip at lower testing temperatures are complimentary trends.
Brittle point fraction analysis was performed in conjunction with pct. shear lip results, as it was of concern that pct. shear lip may not be completely representative of fracture surface morphology. For example, typical pct. brittle or pct. ductile analyses performed on Charpy V-notch fracture surfaces can exhibit what is considered 100 pct. ductile fracture without the entire fracture surface being consumed by shear lips. That is, shear lip area does not represent the entirety of a ductile fracture surface. Therefore, analysis was performed to determine the percentage of microscopic ductile and brittle morphologies on the fracture surface of specimens tested at room temperature. The analysis was performed at regular positions along each fracture surface (section 3.8) and did not include analyzing the microscopic fracture morphologies associated with the shear lips. Justification for not performing standard pct. brittle/ductile analyses dictated by ASTM E23 [66] is presented in section 3.8.1. Micrographs used in the process of determining BPF are presented in Appendix M.

Figure 4.10 Images of Charpy V-notch fracture surfaces for tempering conditions of 1 and 3600 s at a tempering parameter of 13,000 tested at room temperature and -100 °C.

4.2.4 Brittle Point Fraction of CVN Fracture Surfaces

Brittle point fraction analysis was performed in conjunction with pct. shear lip results, as it was of concern that pct. shear lip may not be completely representative of fracture surface morphology. For example, typical pct. brittle or pct. ductile analyses performed on Charpy V-notch fracture surfaces can exhibit what is considered 100 pct. ductile fracture without the entire fracture surface being consumed by shear lips. That is, shear lip area does not represent the entirety of a ductile fracture surface. Therefore, analysis was performed to determine the percentage of microscopic ductile and brittle morphologies on the fracture surface of specimens tested at room temperature. The analysis was performed at regular positions along each fracture surface (section 3.8) and did not include analyzing the microscopic fracture morphologies associated with the shear lips. Justification for not performing standard pct. brittle/ductile analyses dictated by ASTM E23 [66] is presented in section 3.8.1. Micrographs used in the process of determining BPF are presented in Appendix M.
Brittle point fraction (BPF) was determined for all time conditions at 11,000 and 12,000 TP (300 and 350 °C for 3600 s equivalent tempers) for CVN specimens tested at room temperature. Tempering parameters of 11,000 and 12,000 were chosen as TME is most pronounced at these tempering parameters. Table 4.1 displays the BPF values and relative accuracy (see Equation 3.4) associated with each measurement. Figure 4.11 depicts BPF with respect to time on a log scale. Brittle point fraction is shown to decrease with decreasing tempering time for a constant tempering parameter. That is, as tempering time decreases at a constant tempering parameter, a higher fraction of ductile fracture features is exhibited on CVN fracture surfaces. This trend is observed for both 11,000 and 12,000 TPs, although it is more pronounced as the tempering parameter increases from 11,000 to 12,000. Figure 4.11b displays the standard deviation associated with each BPF measurement. Considering variation in measurement, the 1 s condition exhibits the most significant change in BPF in relation to other time conditions, as well as the transition from 11,000 to 12,000 TP.

The change in BPF associated with tempering time at a given tempering parameter indicates increased ductile fracture at shorter tempering times. This trend of increasing ductile fracture with decreasing tempering time at an equivalent tempering parameter is consistent with the room temperature toughness properties presented in section 4.2.1. For a given tempering parameter (11,000 or 12,000 TP), shorter tempering times exhibit increased toughness accompanied by increased ductile fracture, as exhibited by the BPF results shown here. Given ductile fracture typically requires more energy to occur than brittle fracture, a corresponding increase in impact energy with a greater fraction of ductile fracture is not unexpected.

A decrease in BPF with increasing TP, as evident in Figure 4.11, implies an increase in ductile fracture as the degree of tempering is increased. The magnitude of the decrease in BPF with TP varies for the different tempering conditions, where a larger decrease in BPF with TP is observed for shorter tempering times. This behavior indicates that for the same change in degree of tempering (as defined by the tempering parameter), shorter tempering times produce a greater increase in ductile fracture than longer tempering times.

Table 4.1 Brittle Point Fraction and % Relative Accuracy Values for Room Temperature Data Points

<table>
<thead>
<tr>
<th>Approximate Tempering Parameter</th>
<th>Time</th>
<th>Tempering Temperature</th>
<th>Testing Temperature</th>
<th>n</th>
<th>Average BPF</th>
<th>% Relative Accuracy</th>
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<tr>
<td>11000</td>
<td>1</td>
<td>427</td>
<td>RT</td>
<td>4</td>
<td>0.377</td>
<td>18.08</td>
</tr>
<tr>
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<td>386</td>
<td>RT</td>
<td>4</td>
<td>0.415</td>
<td>19.73</td>
</tr>
<tr>
<td>11000</td>
<td>100</td>
<td>350</td>
<td>RT</td>
<td>4</td>
<td>0.463</td>
<td>7.54</td>
</tr>
<tr>
<td>11000</td>
<td>3600</td>
<td>300</td>
<td>RT</td>
<td>4</td>
<td>0.515</td>
<td>19.61</td>
</tr>
<tr>
<td>12000</td>
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<td>RT</td>
<td>7</td>
<td>0.155</td>
<td>23.50</td>
</tr>
<tr>
<td>12000</td>
<td>10</td>
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<td>4</td>
<td>0.354</td>
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</tr>
<tr>
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<td>404</td>
<td>RT</td>
<td>4</td>
<td>0.443</td>
<td>13.68</td>
</tr>
</tbody>
</table>
A decrease in BPF with increasing TP, as evident in Figure 4.11, implies an increase in ductile fracture as the degree of tempering is increased. The magnitude of the decrease in BPF with TP varies for the different tempering conditions, where a larger decrease in BPF with TP is observed for shorter tempering times. This behavior indicates that for the same change in degree of tempering (as defined by the tempering parameter), shorter tempering times produce a greater increase in ductile fracture than longer tempering times.

### 4.3 Tensile Testing

Tensile tests were conducted for each tempering condition to determine any change in tensile properties with respect to tempering time condition. Tensile curves, UTS, YS, and reduction of area data are presented and discussed in this section.

#### 4.3.1 Tensile Curves

Figure 4.12 displays stress-strain results for the various tempering conditions. Tempering parameter and equivalent 3600 s tempering treatment are displayed in the lower right corner of Figure 4.12a through Figure 4.12d. The equivalent 3600 s tempering treatment designation, such as “3600 s - 200 °C EQ”, indicates that all tempering time conditions included in the figure were tempered to be equivalent to a tempering operation of 3600 s at 200 °C. It should be noted that any jogs in
Figure 4.12 well beyond yielding are an artifact of resetting the extensometer. The 10 s condition at a tempering parameter of 9,000 fractured at the knife edge of the extensometer, the location of fracture is thought to contribute to the reduced post-uniform elongation. Overall, it is evident from Figure 4.12 that tensile strength decreases and elongation increases with increasing tempering parameter.

Figure 4.13 displays stress-strain yielding behavior for tempering parameters of 11,000 – 13,000 for all time conditions examined. At certain tempering parameters, both the 100 and 3600 s conditions exhibit a discontinuity in the stress-strain curve upon yielding, while the 1 and 10 s conditions exhibit no such incipient yielding or yield point elongation (YPE). The stress-strain behavior of all the time conditions for TPs of 9,000 and 10,000 did not exhibit any differences in yielding behavior; continuous yielding was observed for each condition.

The yielding behavior exhibited in Figure 4.13 implies a relative decrease in mobile dislocation density for the 100 and 3600 s conditions compared to the 1 and 10 s conditions at an equivalent tempering parameter. A decrease in the population of mobile dislocations is commonly caused by mobile species pinning dislocations or by dislocation recovery. Considering dislocation pinning, given carbon is the most probable mobile species in this alloy, a decrease in the degree of pinning implies either a
decrease in carbon mobility or a decrease in the amount of carbon in solution associated with shorter times at higher temperatures. If it is assumed that more cementite formation and growth leads to a greater degree of austenite decomposition, then the decrease in pinning for the short-time tempers is not a result of less carbon in solution (since shorter tempering times exhibit retarded austenite decomposition compared to longer tempering times, as shown in Figure 4.1). Therefore, assuming a decrease in mobile dislocation density associated with the longer tempering times, the inflection in the stress-strain data (Figure 4.13) for the 100 and 3600 s conditions at TPs of 11,000 to 13,000 might be attributed to a relative increase in carbon diffusion or an increase in dislocation recovery during tempering compared to the 1 and 10 s conditions.

The mechanisms discussed above were in the context of a relative decrease in mobile dislocation density associated with longer tempering times; however, the behavior exhibited in Figure 4.13 could also be considered in the context of a relative increase in mobile dislocation density associated with shorter tempering time conditions. That is, the yielding behavior could be the result of shorter tempering times experiencing a higher degree of dislocation generation during heating and quenching processes associated with tempering. A possible mechanism for dislocation introduction during tempering is the transformation of retained austenite to fresh martensite during quenching from the tempering temperature. During tempering, retained austenite can be depleted of carbon via carbide formation, thereby decreasing the stability of the remaining austenite. Due to this decrease in stability, fresh martensite may form upon quenching and subsequently increase the mobile dislocation population of the tempered structure. Assuming an increase in mobile dislocation density associated with the shorter tempering times, the inflection in the stress-strain data (Figure 4.13) for the 100 and 3600 s conditions at TPs of 11,000 to 13,000 might be attributed to a lower degree of dislocation generation during tempering compared to the 1 and 10 s conditions.

The yielding behavior in Figure 4.13 suggests a difference in kinetic response between tempering time conditions at a given tempering parameter, assuming the discontinuous yielding behavior is a result of dislocation recovery or carbon diffusion to dislocation cores, as both of these mechanisms are dependent on kinetics. Kinetic differences between tempering time conditions at a constant tempering parameter were also mentioned in section 4.1 with respect to retained austenite decomposition behavior. Retained austenite content and discontinuous yielding results both imply a slower kinetic response during tempering associated with the shorter tempering time conditions at an equivalent tempering parameter.
Figure 4.13  Stress-strain curves for all tempering time conditions and tempering parameters of 11,000, 12,000, and 13,000.
The absence of an inflection point for the 100 s condition at 13,000 TP is noted as an interesting phenomenon, given the explanation developed here, as it seems that increasing tempering parameter would correspondingly increase carbon diffusion to dislocation cores and dislocation recovery, thereby decreasing mobile dislocation density. Despite this inconsistency, the developed arguments involving carbon mobility (to pin dislocations), dislocation recovery, and/or dislocation generation are the most likely scenarios in contributing to the discontinuous yielding behavior displayed in Figure 4.13.

4.3.2 Ultimate Tensile Strength and Yield Strength

Figure 4.14 displays the ultimate tensile strength (UTS) results for each time condition as a function of tempering parameter. Ultimate tensile strength values vary systematically with tempering time, where shorter tempering times yield lower tensile strengths as tempering parameter is increased. The error bars represented in Figure 4.14b signify standard deviation and are useful in determining significant differences in the UTS data. The number of samples used in determining the standard deviation of UTS for each tempering condition can be found in Appendix H, along with the tabulated tensile data. Overall, the mid-range tempering time conditions of 10 and 100 s do not seem to differ significantly from one another. Conversely, the 3600 s condition deviates from the short-time conditions in relation to strength at ~11,000 TP. As tempering parameter increases beyond ~11,000, three distinct strength levels are observed corresponding to 1, 10/100, and 3600 s conditions, where shorter tempering times exhibit lower strength levels.

Figure 4.14 UTS (MPa) as a function of tempering parameter for tempering times of 1, 10, 100, and 3600 s with (a) polynomial fit lines and (b) standard deviation error bars included.
Yield strength (YS) as a function of tempering parameter is presented in Figure 4.15 for each time condition. A systematic decrease in YS is observed with increasing tempering parameter, and shorter time conditions exhibit a greater decrease in YS with tempering parameter. Aided by the displayed standard deviation error bars (number of specimens for each condition in Appendix H), it is observed that the 1 s condition significantly deviates from the 10, 100, and 3600 s conditions at a TP of 12,000. At 13,000 TP, each time condition is distinctly differentiated in terms of yield strength, where decreasing tempering time exhibits lower yield strengths.

Figure 4.15  YS (MPa) as a function of tempering parameter for tempering times of 1, 10, 100, and 3600 s with (a) polynomial fit lines and (b) standard deviation error bars included.

Hardness values for the different tempering time conditions were confirmed to be similar for each tempering parameter in section 3.3.3 (Figure 3.10); however, given the differences in UTS and YS properties exhibited in Figure 4.14 and Figure 4.15, respectively, the effect of slight hardness variation between tempering conditions at a constant tempering parameter must be considered. Figure 4.16 displays UTS (Figure 4.16a) and YS (Figure 4.16b) as a function of hardness for the 1 and 3600 s conditions. Note that hardness is represented on a decreasing axis. The 10 and 100 s conditions were not included as trends and individual data points were more difficult to discern with all conditions represented. The general trends apparent in Figure 4.14 and Figure 4.15, where shorter tempering times typically exhibit lower UTS and YS values at an equivalent tempering parameter, are upheld in Figure 4.16 at an equivalent hardness value. However, UTS and YS variations between tempering time conditions are smaller when represented as a function of hardness. With respect to Figure 4.14 and Figure 4.15, the largest difference between UTS at an equivalent tempering parameter (13,000 TP) with respect to the 1 and 3600 s
conditions is approximately 150 MPa. The largest difference between YS at an equivalent tempering parameter (13,000 TP) with respect to the 1 and 3600 s conditions is approximately 170 MPa. When UTS and YS are compared at an equivalent hardness value, utilizing the extended (dashed) trend lines in Figure 4.16a and Figure 4.16b, the largest difference between the 1 and 3600 s conditions is approximately 90 and 110 MPa, respectively.

Figure 4.17 displays UTS (Figure 4.17a) and YS (Figure 4.17b) as a function of hardness with included standard deviation error bars associated with hardness measurements. In light of the hardness variation exhibited in Figure 4.17, UTS and YS differences between tempering conditions are only significant at a hardness of approximately 50 HRC and lower. This is similar to the behavior discussed above, where the difference in UTS and YS at an equivalent tempering parameter only becomes significant at higher tempering parameters (~12,000 and 13,000). The UTS and YS trends in Figure 4.14 and Figure 4.15 have been shown to remain consistent when UTS and YS are compared at an equivalent hardness level. This confirms that the strength differences observed for the various tempering time conditions are not the result of hardness variations.

The disparity in strength observed for the various tempering time conditions at an equivalent tempering parameter or hardness is difficult to attribute to a single strengthening mechanism without additional microstructural information. One possible contribution to the differences in yield strength is attributed to the yielding behavior observed in Figure 4.13. Longer tempering times at tempering parameters of 11,000 and above were shown to lead to discontinuous yielding. Measured yield strength is often slightly higher for steels that exhibit yield point elongation compared to those that exhibit more roundhouse yielding behavior. The trend of yield strength differences, where longer tempering time conditions at higher tempering parameters exhibit higher yield strengths, is consistent with expectations based on the yielding behavior presented in Figure 4.13. Additionally, changes in cementite and transition carbide size, spacing, and morphology have the potential to affect strength; however, further understanding of the cause of the difference in strength between tempering time conditions requires additional microstructural information.
Reduction of area was measured for each tensile test in which fracture occurred within the region of interest, as defined in Appendix B. Figure 4.18 displays reduction of area as a function of tempering time.

Figure 4.16 (a) UTS (MPa) and (b) YS (MPa) as a function of hardness for tempering times of 1 and 3600 s including polynomial trend lines. Dashed line represents the predicted continuation of the polynomial fit for the 3600 s condition.

Figure 4.17 (a) UTS (MPa) and (b) YS (MPa) as a function of hardness for tempering times of 1 and 3600 s including hardness standard deviation error bars included. Dashed line represents the predicted continuation of the polynomial fit for the 3600 s condition.

4.3.3 Reduction of Area

Reduction of area was measured for each tensile test in which fracture occurred within the region of interest, as defined in Appendix B. Figure 4.18 displays reduction of area as a function of tempering time.
parameter (Figure 4.18a) and hardness (Figure 4.18b) for the various time conditions, where hardness is represented on a decreasing axis. Reduction of area (corresponding to ductility) is shown to increase with decreasing tempering time at an equivalent tempering parameter/hardness. While the reduction of area data are fairly systematic, the standard deviation associated with each measurement should be noted and considered. Figure 4.19 shows the reduction of area results with corresponding standard deviation for each measurement. Number of samples used in determining the standard deviation of reduction of area for each tempering condition can be found in Appendix H. As seen in Figure 4.19a, most error bars of the various time conditions overlap, with the exception of the 3600 s condition at 300 °C (~11,000 TP).

Figure 4.19b shows a comparison of the 1 and 3600 s conditions, where it is more clear that there is an overall increase in reduction of area with decreased tempering time for these two conditions, particularly at tempering parameters of 11,000 and 13,000. Tempered martensite embrittlement, in addition to manifesting as a trough in impact toughness, can occasionally be identified as a trough in reduction of area. As displayed in Figure 4.19, the 3600 s condition exhibits a trough in reduction of area at 11,000 TP, consistent with the impact energy trough of the 3600 s condition previously presented in sections 4.2.1 and 4.2.2 (Figure 4.5 and Figure 4.8). Given the minimal standard deviation associated with the 3600 s condition, it is reasonable to conclude the trough in reduction of area for the 3600 s condition is real and most likely the result of TME. The 1 s condition, conversely, does not exhibit a trough in reduction of area, illustrating a reduced TME trough with short-time tempering.

Figure 4.18 Reduction of area (%) as a function of (a) tempering parameter and (b) hardness for all tempering time conditions, displayed with linear fits.
At an equivalent tempering parameter, short-time tempering has been found here to decrease tensile (Figure 4.14) and yield strength (Figure 4.15) and increase toughness (Figure 4.5) and ductility (Figure 4.18). Typically, as tensile and yield strength decrease with tempering, there is a corresponding increase in ductility and toughness [81]. To better understand the relationship between strength, toughness, and ductility in this study, room temperature impact toughness is plotted in relation to ultimate tensile strength and yield strength in Figure 4.20. It should be noted that UTS and YS are represented on a decreasing (reversed) axis. At a given UTS and YS level, shorter tempering time conditions are shown to exhibit higher toughness values on average. Yield strength is often related to the resistance of dislocation motion. The trend observed in Figure 4.20b suggests that differences in impact energy between the tempering time conditions are not related to dislocation mobility.

Figure 4.21 displays reduction of area as a function of UTS and YS. As evident from the linear fit lines, shorter tempering times generally exhibit increased reduction of area at an equivalent tensile strength level. Through these comparisons, it is shown that shorter tempering times improve toughness and ductility at an equivalent strength level; therefore, the observed increase in toughness and ductility for shorter tempering times is not simply a result of decreased strength. Figure 4.20 and Figure 4.21 highlight the promise of short-time tempering for improving strength-toughness and strength-ductility combinations of tempered martensite.
Time-Temperature Equivalence

Short-time tempering has been shown to improve toughness, diminish TME, and improve ductility when compared to longer tempering times within an equivalent tempering parameter regime. Additionally, through the observed retained austenite decomposition and discontinuous yielding.

Figure 4.20 Impact energy (J) as a function of (a) UTS (MPa) and (b) YS (MPa) with spline and polynomial fit lines included, respectively. Data points are an average of both included parameters (strength and toughness).

Figure 4.21 Reduction of area (%) as a function of UTS (MPa) with linear fit lines included. Data points are an average of both included parameters (strength and reduction of area).

4.5 Time-Temperature Equivalence

Short-time tempering has been shown to improve toughness, diminish TME, and improve ductility when compared to longer tempering times within an equivalent tempering parameter regime. Additionally, through the observed retained austenite decomposition and discontinuous yielding.
behaviors, as well as the overall differences in mechanical properties, a difference in kinetic response has been identified between tempering time conditions at an equivalent tempering parameter. These results bring into question the ability of hardness to broadly represent time-temperature equivalence. In this section, the Hollomon-Jaffe tempering parameter, as well as a more recently proposed method of equating tempering time and temperature, are presented and discussed. The two time-temperature equivalence methods are then compared in the context of the present results.

4.5.1 Hollomon-Jaffe Tempering Parameter

In their original paper, Hollomon and Jaffe [19] chose hardness to represent the “degree of tempering” due to its ease of measurement and already wide use as an indicator for degree of tempering. However, Hollomon and Jaffe’s work, as well as many others [19, 24, 82], came to focus on developing a strategy for tempering steels at varying temperatures and times to produce equivalent hardness values, rather than to produce equivalent microstructures or fundamental kinetic behaviors. This produces an issue when equivalent hardness can be obtained via different microstructural evolution paths and different stages of tempering development. Thus, it should be recognized that the Hollomon-Jaffe tempering parameter is a tool for obtaining equivalent hardness, rather than an equivalent degree of tempering.

The assumption that hardness accurately represents degree of tempering is ubiquitous in literature, and may be the result of inconsistencies in the tempering parameter that are often overlooked, such as c-value variation and deviation from classical diffusion equations inherent to the tempering parameter. The Hollomon and Jaffe tempering parameter relates time, temperature, and relative hardness through the expression:

\[
\text{Hardness} = f[T(\log t + c)]
\]

\[
\text{Tempering Parameter} = T(\log t + c)
\]

where \(T\) is absolute temperature, \(t\) is time, and \(c\) is a constant related to the steel used. While this method is widely used for determining time-temperature equivalence, it was mentioned in section 2.2 and further covered in Appendix A that Hollomon and Jaffe first stated \(c\) only varies with carbon content, while later studies reported an inconsistency in the c-value “constant” for equivalent carbon contents [20].

Thomas et al. pointed out [22] that Hollomon and Jaffe first assumed that hardness would correlate with the regular form of diffusion equations, where hardness would be a function of 

\[
(t \times \exp \left(-\frac{Q}{RT}\right)).
\]

However, they discovered that the apparent activation energy \(Q\) varied with hardness. From this point, they settled on utilizing an activation energy value that varied with hardness and determined that the expression \((t \times \exp \left(-\frac{Q}{RT}\right))\) would remain constant for all hardness values. However, traditional diffusion equations employ a constant activation energy and the extent of diffusion, or the
expression \( t \ast \exp \left( - \frac{Q}{RT} \right) \), typically increases with temperature and time. The variation in the “constant” c-value, as well as deviations from the expected diffusion behavior, result in an equivalent time-temperature indicator, hardness, that is somewhat empirical and not completely based on fundamentals.

Due to the empirical nature of the Hollomon-Jaffe tempering parameter, as well as the observed differences in mechanical properties and kinetic response at an equivalent hardness value, it stands to reason that it may be advantageous to consider a more fundamental time-temperature relationship, particularly for short-time tempering applications.

4.5.2 Characteristic Diffusion Distance

As outlined in section 2.2, a fundamental time-temperature approach based on the characteristic diffusion distance associated with the three stages of tempering was proposed by Thomas et al. [22]. Characteristic diffusion distance is represented by:

\[
x_c \approx \sqrt{2Dt}
\quad (4.2)
\]

where \( t \) is time and \( D \) is diffusivity given by the equation:

\[
D = D_0 e^{-\left( \frac{Q}{RT} \right)}
\quad (4.3)
\]

where \( D_0 \) is the pre-exponential frequency factor, \( Q \) is the activation energy for diffusion, \( R \) is the universal gas constant, and \( T \) is the absolute temperature. The activation energy and pre-exponential factor depend on the type of diffusion that occurs in each tempering stage.

The three diffusion distances utilized in this time-temperature relationship are based on the diffusion of carbon in martensite, carbon in austenite, and iron in ferrite for stages I, II, and III, respectively [83–86]. Figure 4.22 displays iso-tempering curves corresponding to equivalent characteristic diffusion distances for each tempering stage, as calculated by Thomas et al. [22]. The stage transitions are defined at 1 hr tempering times, as indicated in the figure. These iso-tempering curves suggest that several tempering stages could operate simultaneously or out of what is considered normal order under some conditions, particularly at short tempering times. Due to the short tempering times employed in this study, it is interesting to consider the possibility of various tempering stages operating under different tempering time conditions (at an equivalent Hollomon-Jaffe tempering parameter). The following section expands on possible implications associated with overlapping tempering stages with relation to the present study.
Figure 4.23 illustrates “iso-tempering” curves calculated based on the Hollomon-Jaffe tempering parameter (Figure 4.23a) and characteristic diffusion distance (Figure 4.23b). Note that these calculations were performed during this study and are independent from those displayed in Figure 4.22, calculated by Thomas et al [22]. The stages of tempering are typically defined by temperature ranges (at 1 hr) of 100-250 °C, 200-300 °C, and 250-350 °C for stages I, II, and III respectively [1]. However, in order to simplify for illustration purposes, tempering stages are represented in Figure 4.23 as 100-200 °C, 200-300 °C, and > 300 °C for stages I, II, and III respectively. The data points shown in Figure 4.23 represent the times and temperatures of the tempering treatments performed in the present study. These times and temperatures were determined using the Hollomon-Jaffe tempering parameter and base temperatures of 200, 250, 300, 350, and 400 °C at 1 hr tempering time. The characteristic diffusion distance was calculated for base temperatures of 100, 200, and 300 °C at 1 hr. As seen in Figure 4.23 multiple “iso-tempering” curves are displayed for temperatures 200 and 300 °C, where tempering stages transition. Equations 4.2 and 4.3 were utilized to determine the characteristic diffusion distances for stages I, II, and III. The activation energy and pre-exponential frequency factor vary depending on the type of diffusion occurring during each stage of tempering, resulting in the separate iso-tempering curves displayed for stages I, II, and III in Figure 4.22 and Figure 4.23b.
Stage I involves the formation of transition carbides and the lowering of the carbon content of the matrix martensite to about 0.25% [1]. The progression of stage I is controlled by the diffusion of carbon through martensite with an activation energy of approximately 67 J/mol [15]. As the study that reported this activation energy did not also include a value for the pre-exponential factor, the activation energy (~84 kJ/mol) and pre-exponential factor (0.02 cm$^2$/sec) associated with the diffusion of carbon through ferrite was used for the present characteristic diffusion distance calculations [87]. It should be noted that the “iso-tempering” curves of stage I in Figure 4.22 and Figure 4.23b do not coincide due to a difference in the activation energy employed for the calculations. While Thomas et al [22] indicated that the activation energy and pre-exponential factor for the diffusion of carbon in ferrite was used to determine the iso-tempering curves displayed in Figure 4.22, the calculations performed in the present study suggest that the activation energy and pre-exponential factor used in Thomas’s study were actually associated with the diffusion of carbon in martensite (~67 kJ/mol) and the diffusion of carbon in ferrite (0.02 cm$^2$/sec), respectively.

Stage II involves the decomposition of retained austenite to ferrite and cementite and is controlled by the diffusion of carbon in austenite. The activation energy associated with the diffusion of carbon in austenite is approximately 134 kJ/mol with a pre-exponential frequency factor of 0.15 cm$^2$/sec [85, 86].

Stage III is recognized as the replacement of transition carbides and low-carbon martensite by cementite...
and ferrite. Stage III is associated with the self-diffusion of iron in a ferrite matrix, with an activation energy of 252 kJ/mol and a pre-exponential factor of 5.4 cm²/sec [17].

Figure 4.23 illustrates the relationship between tempering temperature, tempering time, and tempering stage with respect to iso-tempering curves calculated according to the Hollomon-Jaffe tempering parameter (Figure 4.23a) and the characteristic diffusion distance (Figure 4.23b). While Figure 4.23 shows a clear separation and ordering of the tempering stages, Figure 4.23b indicates a more complex relationship between temperature, time, and tempering stage. Comparing the time-temperature combinations with respect to tempering stage in Figure 4.23a and Figure 4.23b reveals differences in the predicted operating tempering stage. For example, the time-temperature combinations associated with the base tempering treatment of 3600 s at 300 °C (denoted by stars in Figure 4.23) will be considered. These time-temperature combinations correspond to a tempering parameter of 11,000 and the minimum of the TME trough. Figure 4.23a shows all time-temperature combinations associated with the base tempering treatment of 3600 s at 300 °C to be at the transition of stage II and III. Conversely, Figure 4.23b indicates that the 3600s condition is at the transition of stage II and III, the 10 and 100 s conditions fall within the stage II + III region, and the 1 s conditions is within the stage I + II + III region. The differences in predicted operating tempering stage when utilizing different time-temperature relationships is significant to the present study. Time-temperature combinations were determined utilizing the Hollomon-Jaffe tempering parameter and assuming tempering stage behavior similar to that of Figure 4.23a. However, Figure 4.23b suggests that the time-temperature combinations employed may experience different operating tempering stages for a constant tempering parameter.

In addition to the possibility of variation in operating tempering stage with tempering time conditions, the comparison between iso-tempering curves in Figure 4.23 provides a basis for the suspected difference in kinetic behavior between tempering time conditions at an equivalent tempering parameter reflected in the earlier discussion of microstructural (retained austenite) and mechanical (discontinuous yielding) properties. Figure 4.24 displays a comparison of tempering parameter and characteristic diffusion distance of the three tempering stages for tempering times relevant to this study. The data points are associated with the specific time-temperature combinations used in the present study and have been converted to tempering parameter and characteristic diffusion distance. Characteristic diffusion distance was calculated utilizing Equations 4.2 and 4.3, the appropriate activation energies and pre-exponential factors for each tempering stage, and the tempering times and temperatures (Table 3.2) employed in the present study.

Figure 4.24 suggests that, while the time-temperature combinations were designed to have equivalent tempering parameters and hardness values, the diffusion distances associated with each tempering stage vary significantly for a given tempering parameter. For stages I and II, longer tempering
times exhibit significantly higher carbon diffusion distances for an equivalent tempering parameter. Conversely, stage III does not indicate large differences in iron self-diffusion distances for the various time conditions at equivalent tempering parameters. Figure 4.24 supports the conclusions pertaining to kinetic behavior that were drawn in sections 4.1 and 4.3.1 with respect to retained austenite and discontinuous yielding behavior. In these sections, shorter tempering times were concluded to exhibit slower kinetics compared to longer tempering times at an equivalent tempering parameter. The slower kinetic behavior associated with shorter tempering times is apparent in Figure 4.24, where shorter tempering times exhibit shorter carbon diffusion distances for a given tempering parameter.

Figure 4.24 Characteristic diffusion distance as a function of tempering parameter for tempering times of 1, 10, 100, and 3600 s for tempering stages (a) I, (b) II, and (c) III.
Figure 4.25 displays the progression of retained austenite content for the 1 and 3600 s time conditions when compared to both tempering parameter and characteristic diffusion distance. Retained austenite content (Figure 4.1) was observed to decrease more gradually with tempering parameter as tempering time is decreased. When retained austenite content is compared in relation to the characteristic diffusion distance of carbon in austenite (Figure 4.25b), the discrepancy between short and long-time tempers is not as severe, where the largest difference is approximately 1 % between time conditions and many error bars overlap. Retained austenite content is a particularly useful metric to compare tempering parameter and (stage II) characteristic diffusion distance, since the decomposition of retained austenite is largely dependent on the diffusion of carbon through austenite (which corresponds to the activation energy of stage II tempering).

Figure 4.25  (a) Retained austenite (vol %) as a function of tempering parameter for tempering time conditions of 1 and 3600 s with included error bars representing standard deviation. (b) Retained austenite (vol %) versus stage II characteristic diffusion distance (cm) for time conditions of 1 and 3600 s, including error bars representing standard deviation.
CHAPTER 5
SUMMARY AND CONCLUSIONS

This chapter presents the primary observations and conclusions relevant to the effects of short time tempering on the mechanical and microstructural behavior of AISI 4340 steel.

Microstructural results indicate a retardation in austenite decomposition with tempering parameter for shorter tempering times. A corresponding diminishment of the TME trough and overall increase in room temperature toughness with shorter tempering times suggests a relationship between the observed austenite decomposition and toughness behavior. As TME is typically associated with the decomposition of retained austenite to interlath cementite, it is likely that the retained austenite decomposition behavior exhibited in this study has a significant effect on cementite nucleation and growth in a manner that serves to diminish TME.

Room temperature toughness data were supported by ductile-to-brittle-transition-temperature (DBTT), pct. shear lip, and brittle point fraction (BPF) results. Transition temperature was shown to decrease systematically with shorter tempering times at an equivalent tempering parameter. Additionally, the DBTT peak (indicating TME) associated with the 3600 s condition was observed to diminish with decreasing tempering time within the same tempering parameter regime. The percentage of shear lip area associated with Charpy fracture surfaces was shown to increase with shorter tempering times at a given tempering parameter. These results, coupled with BPF data, revealed a higher fraction of ductile fracture associated with shorter tempering times at an equivalent tempering parameter. The trends of improved transition temperature and increased ductile fracture features associated shorter tempering times are complementary and further support the room temperature toughness results.

In addition to improved toughness properties, shorter tempering times were associated with increased ductility and decreased strength when compared to longer tempering times at an equivalent tempering parameter. Given that lower strength materials are often accompanied by an increase in toughness and ductility, the relationship between strength and ductility/toughness for the various tempering time conditions was investigated. It was shown that shorter tempering times exhibited an increase in ductility and toughness at a given strength or hardness level when compared to longer tempering times. These relationships confirmed that the toughness and ductility trends were not the result of the slightly decreased strength that was found at shorter tempering times.

Appropriate time-temperature combinations were determined based on the Hollomon-Jaffe tempering parameter, in an attempt to compare properties between tempering time conditions at an “equivalent degree of tempering.” However, despite equivalent hardness at a given tempering parameter, a difference in kinetic behavior between the tempering time conditions at an equivalent tempering parameter was identified via retained austenite, discontinuous yielding, and overall mechanical property
behavior. Some time-temperature combinations utilized in the present study, when considered within the context of characteristic diffusion distance, were shown to fall within regions of overlapping tempering stages, or where tempering stages may operate out of what is considered their “normal” order. Comparing tempering parameter and characteristic diffusion distance of time-temperature combinations utilized in the present study revealed greater carbon diffusion distances associated with longer tempering times at an equivalent tempering parameter (for stages I and II). Therefore, hardness was shown not to be a complete indicator of time-temperature equivalence, and additional fundamental understanding of time-temperature relationships is needed.
CHAPTER 6
FUTURE WORK

This chapter outlines possible focal points for future work pertaining to short-time tempering with relation to TME.

- Mechanical properties associated with short-time tempering proved to be desirable; however, there is a current lack of supporting evidence and understanding surrounding the mechanisms responsible for the observed behavior. Further microstructural analysis and confirmation of the presented retained austenite results is needed to discern, beyond conjecture, the underlying microstructural changes contributing to the presented mechanical properties. Such studies would likely include transmission electron microscopy and Mössbauer spectroscopy.

- Short-time tempering has been shown to improve toughness properties within the TME tempering regime in laboratory resistive heating studies. It may also be of interest to explore the parameters, challenges, and effects of executing short-time induction tempers at an industrial simulation level.

- The effects of short-time tempering on mechanical and microstructural behavior were investigated for AISI 4340, indicating improved ductility and toughness compared to conventional tempering techniques. The effect of alloying is presently unknown and may be important in understanding microstructural development during short-time tempering. Specifically, the effect of alloying additions that influence the formation and growth of cementite, such as silicon, may be of interest to investigate.

- AISI 4340 was chosen to investigate the effects of short-time tempering on mechanical and microstructural behavior in this study due to its availability, prevalence within the literature, and interest to the proposing sponsor. Work focusing on other steel grades, particularly of interest to the industrial community in the context of strength-toughness properties within the TME tempering regime, may be of interest.

- This investigation focused on the effects of tempering hold-time, contrary to many of the recent studies that stress the importance of heating rate and tempering hold-time. Understanding the effect of heating rate within the TME regime may assist in determining the microstructural development occurring at short tempering times while potentially further improving mechanical properties.

- Hardness was shown to be an inadequate indicator of time-temperature equivalence, bringing the use of the Hollomon-Jaffe tempering parameter to represent time-temperature equivalence into question. Further investigation exploring potential alternatives to the Hollomon-Jaffe tempering
parameter is needed to determine a more representative relationship for time-temperature equivalence in the context of short-time and long-time tempers.
REFERENCES


APPENDIX A

EVALUATION OF THE HOLLOMON-JAFFE TEMPERING PARAMETER CONSTANT

It is often assumed that relatively accurate results for equating tempering processes can be obtained by using a general c-value of 16 for steels with 0.25-0.4\%C [19]. Additionally, it is thought that varying the c-value does not impart a significant variation in the final hardness. To support this, Hollomon and Jaffe [19] presented a study in which a difference of 6 in c-value (corresponding to a tempering temperature difference of \(\sim 17^\circ\)C), where c-values typically range from 10 to 20, yielded a difference of about 1.5 HRC. This difference would correspond to a change in tensile strength of approximately 50 MPa for the current material (per analysis technique presented in section 3.3.4).

The c-value for a specific alloy composition is determined by collecting hardness data from a series of heat treatments conducted at a constant tempering temperature and varying times. Figure A.1 shows the isothermal tempering response for temperatures between 500 and 700 \(^\circ\)C reported for a 4340 steel [88]. Temperature and time values at a given hardness are evaluated to produce iso-hardness curves and are displayed in Figure A.2. Based on the TP formulation, the iso-hardness lines all intersect at the same point on the y-axis of Figure A.2, where the y-intercept of the hardness series is denoted as \(\ln(t_o)\) and \(c = -\log(t_o)\).

![Figure A.1 Isothermal tempering response at temperatures ranging from 510 to 691 \(^\circ\)C for a 4340 steel. Data were tabulated from the Semiatin and Stutz [88] study and a logarithmic regression was performed for interpolation.](image-url)
Figure A.3 displays the c-values calculated for each hardness level, as well as the average c-value calculated, 13.7. The c-values are calculated by determining the intercept, \( \ln(t_o) \), for each hardness series and solving for \( c \) using \( t_o \). The two c-values to be considered are therefore 16, from the Hollomon and Jaffe study, and 13.7, from the calculations based on the collected 4340 data of Semiatin and Stutz [88]. In order to determine the impact of the difference in c-values on the tempering treatments for the current work, the two c-values were used in calculating iso-tempering curves. The results are displayed in Figure A.4, where each curve represents an equivalent degree of tempering for various times and temperatures. The base temperatures are presented at the right side of each curve. A base time of 1 hr was used for each iso-tempering curve. The largest difference between the iso-tempering curves for the two c-values is \( \sim 25 \, ^\circ \text{C} \) for a 1 s treatment and an equivalent temperature of 400 \( ^\circ \text{C} \).

Murphy and Woodhead conducted a study in which they evaluated the validity of a variety of tempering parameters, including the Hollomon-Jaffe tempering parameter [82]. During this study, a 0.4% C steel was used to examine the variation of the c-value with hardness using the same procedure as that above. The results are displayed in Figure A.5. When examining the same hardness range evaluated in Figure A.3, 20-45 HRC (\( \sim 240-445 \) VPN), the average c-value is approximately 15.9. Given the suggested use of a c-value of 16 for steels containing 0.25-0.4% C by Hollomon and Jaffe, as well as the Murphy and Woodhead study results, the present work employed a c-value of 16 for all tempering parameter calculations.
Figure A.3  C-value versus hardness (Rockwell C) with displayed average C-value of 13.7.

Figure A.4  Iso-tempering curves generated using C-values of 16 (dashed) and 13.7 (solid). Base of 1h tempering time at temperatures of 200, 250, 300, 350, 400 °C as indicated.
Figure A.5 C-value versus hardness (VPN) for 0.4%C steel. Adapted from [82].
APPENDIX B

CHARACTERIZATION OF TENSILE BLANK THERMAL GRADIENT

When utilizing resistive heating employed by the Gleeble® 3500, a thermal gradient is created along the length of the heated sample and results in a non-uniformly tempered specimen. Typically, the desired temperature is achieved where the control thermocouple is placed (in this case the mid-length of the specimen) and temperature decreases moving away from the mid-length of the specimen toward the gripped ends. The thermal gradient associated with tempering the Charpy blanks was of less concern than the tensile blanks, since the local properties at the notch will not be affected by non-uniform tempering far from the notch.

In order to achieve a more uniformly tempered specimen, the thermal gradient can be minimized, particularly for the section of material that is to be mechanically tested. Jaw-type, peak temperature, specimen diameter, and free span can all be adjusted in order to reduce the thermal gradient. Typically, the thermal gradient decreases with decreasing peak temperature and increasing free span (distance between Gleeble grips). Stainless steel jaws produce a less pronounced thermal gradient than copper jaws for steel samples. Thermal profile characterization tests were conducted using stainless steel jaws, a free span of 100 mm, and 10 mm diameter samples. The free span length was chosen, as to minimize the thermal gradient. A free span of 100 mm is approaching the longest free span physically possible to achieve using the Gleeble. A 10 mm diameter cylindrical sample was chosen due to stock material and Gleeble jaw availability.

Tests were conducted to characterize the thermal profile and to establish a region of relatively uniform tempering to serve as the tensile specimen gauge length. After initial testing, it was evident that the 1 and 10 s tempers did not provide enough dwell time for the thermal gradient to fully manifest. The thermal gradient is a product of heat transfer from the sample to the water-cooled grips. For such short tempering times, there was very limited time for heat transfer. Therefore, the temperature along the length of the sample for the 1 and 10 s tempers only differed by a few degrees. For this reason, the 100 s temper was chosen to define the thermal gradient. Since higher temperatures generally produce a more severe thermal gradient across the sample, the highest temperature associated with the 100 s temper, 458 ºC, was chosen for these tests.

Figure B.1a displays the time-temperature profile of the 100 s, 458 ºC tempering treatment. Thermocouples were placed at the mid-length of the specimen as well as 5 mm, 10 mm, and 15 mm away from the mid-length. Figure B.1b illustrates the thermal gradient associated with the thermal profiles in Figure B.1a immediately before quenching. The temperature at the grips is assumed to be approximately 30 ºC.
The equivalent isothermal tempering time (section 2.2.2) at each monitored position of the specimen was calculated to assist in determining an acceptable tensile specimen gage length. This is a similar process to what was performed in section 3.3.4 to evaluate the tempering of the Charpy blanks. The isothermal tempering time was calculated for 458 °C with a c-value of 16. To better understand the acceptable deviance from the desired isothermal tempering time, the equivalent tempering times for each position were used to calculate the experimental tempering parameter. These values were then compared to the aim tempering parameter. The same tempering parameter to hardness correlation outlined section 3.3.4 was used to calculate the expected hardness deviation from the desired hardness at each monitored position on the sample. Figure B.2a displays the change in the experimental equivalent isothermal tempering time with distance from the mid-length. The corresponding hardness deviation expected for each position on the sample is illustrated in Figure B.2b. As stated previously in section 3.3.4, a hardness deviation of 0.2 HRC is considered reasonable for this study. A distance of 5 mm from the mid-length of the sample, or 10 mm total gage section, allows for an acceptable hardness deviation and was therefore used as a gage length basis in the design of the tensile specimen geometry. This gage length corresponded to a tempering temperature “range” of only a few degrees.
Figure B.2  (a) Equivalent tempering time versus distance from mid-length and (b) hardness deviation versus distance from mid-length.
APPENDIX C
HEATING RATE DURING TEMPERING

Variation in heating rate during tempering has been proposed to affect the precipitation kinetics of cementite during tempering, as discussed in section 2.7 [11.26–29]. Specifically, studies have linked high heating rates to a finer distribution of cementite. The present study focuses on the effect of short tempering hold times on mechanical properties and microstructural development, specifically related to TME. In order to isolate the effect of short holding times, experiments were designed with the intent of keeping heating rates relatively constant for the shorter tempering times. The 3600 s tempers were conducted in salt pots and, therefore, experienced a slower heating rate than the 1, 10, and 100 s tempers.

Short-time tempers (1, 10, 100 s) were programmed with a heating rate between 1200 and 1400 °C/s. These values were arbitrarily chosen with the intent that the Gleeble would reach the highest achievable heating rate, but would most likely not accomplish the programmed heating rate. After all tempering heat treatments were performed, the time-temperature profile of each heat treatment was evaluated in order to determine the actual heating rate of the tempering operations. Figure C.1 displays the heating rates associated with the 1, 10, and 100 s conditions for all Charpy tempers, where the heating rate was unexpectedly found to increase with holding temperature from approximately 725-975 °C/s. Due to this relationship, heating rate is also shown to increase with decreasing hold time, as displayed in Figure C.2. This, initially, seems to present an issue in isolating the effect of holding time on the mechanical properties and microstructural development. This behavior was only detected in Charpy heat treatments. For the tensile heat treatments, a relatively constant heating rate ranging from ~600-660 °C/s was maintained with no systematic variations.

The cause of variation in heating rate observed in the Charpy tempering operations is thought to be a combination of two factors: power output and material resistivity. Power output is an import aspect to heat treating in the Gleeble, since it is closely linked to the current that passes through the sample. As current passes through the sample, heat is generated due to the resistivity of the sample material. At maximum power output, current is also at a maximum; therefore, heat is generated within the sample at a faster rate compared to lower power outputs. From this relationship, it can be concluded that the maximum achievable heating rate for a particular sample is achieved when the power output is at a maximum. When attempting to achieve the highest heating rate possible, the Gleeble system increases power output until the maximum value is met; however, this process takes a certain amount of time (~0.17 s). Therefore, during the initial 0.17 s of heating, the maximum achievable heating rate is not being met, since power output is not at a maximum. Due to this, lower holding temperatures experience slower heating rates since a large percentage of the time to heat is not spent at the maximum power output. For example, for a low holding temperature, it may take ~0.3 s to reach the desired tempering temperature;
therefore, ~57% of heating time is not spent at the maximum achievable heating rate. This, in turn, produces an overall slower heating rate.

Figure C.1  Heating rate as a function of tempering temperature for tempering times of 1, 10, and 100 s; where each datum is an average of 7 values.

Figure C.2  Heating rate as a function of parameter for tempering times of 1, 10, and 100 s; each data point is an average of 7 values with standard deviation error shown.

The power output explanation seems to be valid for low holding temperatures; however, as holding temperature increases and the percentage of time spent at the maximum achievable heating rate during heating increases, it seems that this maximum heating rate would dominate the curve and heating
rate would trend toward some constant as temperature continued to increase. This is not the behavior observed in Figure C.1, where heating rate continues to increase with holding temperature. Therefore, there is some other mechanism causing this behavior: the variation of material resistivity with temperature. An increase in temperature is accompanied by a corresponding increase in material resistivity. In the Gleeble system, an increase in test material resistivity will render an increase in the sample’s ability to generate heat when a certain amount of current is passed through. Therefore, it would be expected that with an increase in tempering temperature, a corresponding increase in heating rate would be observed.

While power output and resistivity can be used to explain the observed variation in heating rate with holding temperature for the Charpy specimen heat treatments, a detailed understanding as to why the same variation is not observed in the tensile specimen heat treatments has not been developed. Most likely, sample geometry plays a role in the heating rate behavior. During the process of experimental design, variation in heating rate was not considered; however, it has been found that as the programmed heating rate is increase, power output and resistivity effects are amplified.

In order to determine the effect of varying heating rates on mechanical properties, additional Charpy blanks were tempered at a consistent heating rate of 650 °C/s to be consistent with the heating rates observed for the tensile blank tempers. Short-time conditions (1, 10, 100 s) at the highest TP value (~13000) were investigated. These conditions were chosen on the basis that the heating rates at this TP, displayed in Figure C.2, differ most greatly from 650 °C/s. Two specimens were tempered for each condition to arrive at a total of 6 specimens dedicated to the heating rate study. It should be noted that the change in heating rate from the original heating rates to the consistent heating rate of 650 °C/s did not significantly affect the equivalent times; therefore, the same hold times were utilized for the 650 °C/s tempers, as was used for the faster heating rate tempers.

Figure C.3 compares the CVN energy results of the consistent and variable heating rate specimens. The data points displayed in Figure C.3 that correspond to the 650 °C/s specimens are an average of two values. The 650 °C/s specimens exhibit slightly lower values than the variable heating rate specimens; however, the differences do not exceed the expected variation observed in the original specimens, where energy values often varied up to 1 ft-lb in difference. This is true for both the averaged 650 °C/s specimen energy values as well as for the individual values, where the largest difference between the variable heating rate specimens and the 650 °C/s specimens is 1 ft-lb. Therefore, the differences in heating rate for the short-time tempers is not thought to significantly affect the mechanical properties. It is thus valid to analyze the results in this study solely as a factor of hold time in relation to the short-time tempers. Heating rate effects cannot, however, be ignored when comparing the conventional and short-time tempers.
While short-time tempers were executed with relatively equivalent heating rates, the 3600 s tempers experienced much slower heating rates compared to the short-time tempers, since the 3600 s tempering treatments were performed in salt pots. For this reason, heating rate effects should be considered when comparing the 3600 s condition to any of the short-time tempering conditions. If heating rate were considered to have a more pronounced effect on mechanical and microstructural behavior than holding time, it would be expected that the 1, 10, and 100 s tempers would all exhibit similar properties. However, as observed in the present results, there are consistent, systematic trends observed with relation to tempering hold time rather than heating rate. This behavior indicates that the differences in heating rate between the conventional and short-time tempers did not have a controlling influence on the microstructural and mechanical properties observed in this study.

Figure C.3 Impact energy (J and ft-lbs) as a function of tempering parameter for tempering times of 1, 10, and 100 s. Data denoted by X’s associated with the specimens heated at a heating rate of 650 °C/s.
APPENDIX D
FINAL TENSILE GEOMETRY DESIGN PROCESS

As discussed in Appendix B, a gage length of 10 mm captures a region of relatively equivalent tempering temperature. Due to the difficulty associated with machining material at hardness levels of 45 – 60 HRC, the smallest ASTM standard sub-size round tensile specimen, with a gage section of 10 mm and reduced cross-section diameter of 2 mm, could not be produced [69]. Alternatively, tensile geometry design was based on Specimen 4 of “test specimens with gage length four times the diameter” in ASTM E8 [69]. Figure D.1 displays the chosen tensile specimen geometry, with a 16 mm gage length within the 20 mm reduced cross-section. This specimen was chosen with the intent of using a 10 mm extensometer to capture the strain behavior within the region of interest.

An error during the machining process led to the necessary adaptation of the proposed tensile geometry. Machining errors manifested in a shifting of the specified reduced cross-section away from the mid-length of the tensile blank and resultantly did not include the region of interest within the reduced cross-section. In order to correct for this, the reduced cross-section was extended from the original 20 mm to a length of 60 mm for all short-time tempered specimens. Prior to this correction, the 10 mm region of interest was located on the fillet region of the specimen and would not have produced accurately representative tensile results. Figure D.2 illustrates the originally proposed geometry, the incorrectly machined geometry, and the adapted geometry. The conventionally tempered, 3600 s specimens were left with the original 20 mm gage length since the location of the reduced cross-section was not imperative. Additionally, 10 extra tensile blanks were heat treated in accordance with the 1 s tempering conditions. These 10 blanks were then sent out to be machined as originally intended, featuring the 20 mm gage length. The extra samples were created with the intention of increasing the likelihood of collecting data in which fracture would occur within the 10 mm extensometer range and to compare the 20 mm and 60 mm gage length results to note any significant differences as a result of the specimen geometry. Failures occurred in the gage sections of the modified specimens, and no systematic differences were observed between the two specimen geometries for a given tempering condition.
Figure D.2 Illustration of original, machined, and adapted tensile specimens for short-time tempering conditions. Not to scale.
Due to the nature of resistive heating, along with the high heating rates utilized during this study, significant thermal overshoot was often observed during tempering in the Gleeble. In order to avoid such overshoots, manual adjustments were made to the programmed temperature profile. The Gleeble® Users Training handbook [89] suggests a method outlined in Figure E.1, where the temperature difference of the thermal overshoot, $\Delta T$, is subtracted from the desired temperature and the system is programmed to hold for approximately 1/3 of the time of the overshoot. This method was used to correct the thermal overshoots observed in tensile blank preliminary testing. Figure E.2 shows a comparison of an original program with an adjusted program to account for overshoot. The original program, set to isothermally hold at 600 °C, exhibits an overshoot of approximately 10 °C and does not reach the desired temperature by the end of the treatment. By using the method for eliminating overshoot, the adjusted program achieves an actual thermal profile much closer to the desired isothermal hold.

Figure E.1  Illustration of technique outlined in the Gleeble® Users Training handbook for correcting thermal overshoot [89].
Figure E.2  Comparison of the original versus the adjusted thermal profile for a 10 s, 600 °C tempering treatment, showing programmed and measured thermal profiles.
Preliminary Gleeble heat treatments revealed a delay, typically less than 0.5 s, between the programmed and actual start of heating. While a delay of this time would typically be inconsequential, the short time conditions of the present thermal treatments required that the delay be considered. In order to account for the observed delays, the hold time was simply extended to offset the time lost during the delay. Figure F.1 qualitatively depicts the effect of extending the treatment hold time on the relationship between the programmed and actual thermal profiles. The issue of this delay was only taken into account, and considered relevant for the 1 and 10 s tempers. The actual extended times are tabulated in Appendix G.

Figure F.1 Illustration of the effect of extending the treatment hold time on the relationship between the programmed and actual thermal profiles.
APPENDIX G
QUICKSIM2 PROGRAMS

QuickSim2 programs were employed to control the short-time Gleeble tempers. The location of time and temperature parameters within the 1, 10, and 100 s programs is outlined in Figure G.1 through Figure G.3. The illustration of these parameters with respect to time-temperature profiles is displayed in Figure G.4 to Figure G.6. Time and temperature parameters are tabulated in Table G.1.

![Figure G.1 Illustration of parameters $t_1$, $t_2$, and $T_1$ for all 1 s programs. An illustration of these parameters with respect to the time-temperature profile is shown in Figure G.4.](image-url)
Figure G.2 Illustration of parameters $t_1$, $t_2$, $t_3$, $t_4$, $T_1$ and $T_2$ for all 10 s programs. An illustration of these parameters with respect to the time-temperature profile is shown in Figure G.5.
Figure G.3 Illustration of parameters $t_1$, $t_2$, $t_3$, $t_4$, $T_1$ and $T_2$ for all 100 s programs. An illustration of these parameters with respect to the time-temperature profile is shown in Figure G.6.
Figure G.4 Illustration of parameters $t_1$, $t_2$, and $T_1$ for all 1 s programs in relation to the programmed and actual time-temperature profile.

Figure G.5 Illustration of parameters $t_1$, $t_2$, $t_3$, $t_4$, $T_1$, and $T_2$ for all 10 s programs in relation to the programmed and actual time-temperature profile.
Figure G.6 Illustration of parameters $t_1$, $t_2$, $t_3$, $t_4$, $T_1$ and $T_2$ for all 100 s programs in relation to the programmed and actual time-temperature profile.
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## APPENDIX H

### TABULATED TENSILE DATA

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</tr>
</tbody>
</table>

* Prefix corresponds to austenization batch

** Sample IDs with prefix “R” are “redo” samples that were introduced to obtain a select number of short-time samples with the originally intended tensile specimen geometry

*** Shaded values indicated fracture outside acceptable range per thermal gradient characterization (outside 10 mm range of consistent tempering from Gleeble specimens). These values were not included in plots throughout the thesis, but should be noted.
APPENDIX I
CHARPY ENERGY TRANSITION FITTING USING BRITTLE POINT FRACTION

As mentioned in section 3.6.1, manually fit curves were constructed when Equation 3.1 was thought to produce an unacceptable fit. To better inform the transition curves adopted for the manually fit energy data that is presented in section 4.2.2, the brittle point fraction (BPF) values for the -200 °C (lowest) and 200 °C (highest) testing temperature conditions were examined. The BPF values were then used to help fit the Charpy curves, particularly relating to the shape of the upper and lower shelves of the manually fit curves. For example, if the 200 °C fracture surface was ~0.99 fraction ductile fracture, then the upper shelf curve was drawn relatively flat. All of the upper shelf results fell into this category. However, considering the lower shelf data, if the -200 °C condition was only ~0.9 fraction brittle, then the lower shelf region was drawn with a slightly positive slope. This infers that a lower testing temperature may yield lower impact toughness values. It should be noted that, due to the quasi-cleavage nature of brittle fracture in these materials, there is some ductility expected to be present at the lower shelf energy associated with tear ridges in the quasi-cleavage fractures. The results of the point fraction analysis are displayed in Table I.1 and Table I.2. The relative accuracy (Equation 3.4) associated with each measurement as well as the number of micrographs measured (n) are also presented. The “upper shelf” of the most ductile points are presented in terms of ductile point fraction (DPF).

Table I.1  Ductile Point Fraction and % Relative Accuracy Values for 200 °C Data Points

<table>
<thead>
<tr>
<th>Time</th>
<th>Tempering Temperature</th>
<th>Testing Temperature</th>
<th>n</th>
<th>Average DPF</th>
<th>% Relative Accuracy</th>
</tr>
</thead>
<tbody>
<tr>
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<td>200</td>
<td>4</td>
<td>0.989</td>
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<td>444</td>
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<td>4</td>
<td>0.985</td>
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</tr>
<tr>
<td>100</td>
<td>458</td>
<td>200</td>
<td>4</td>
<td>0.999</td>
<td>0.40</td>
</tr>
<tr>
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<td>0.998</td>
<td>0.40</td>
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</table>

Table I.2  Brittle Point Fraction and % Relative Accuracy Values for -200 °C Data Points

<table>
<thead>
<tr>
<th>Time</th>
<th>Tempering Temperature</th>
<th>Testing Temperature</th>
<th>n</th>
<th>Average BPF</th>
<th>% Relative Accuracy</th>
</tr>
</thead>
<tbody>
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<td>0.905</td>
<td>2.52</td>
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<tr>
<td>10</td>
<td>444</td>
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<td>4</td>
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<td>0.53</td>
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<tr>
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<td>400</td>
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<td>4</td>
<td>0.918</td>
<td>2.52</td>
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</table>
Data pertaining to impact energy for a variety of testing temperatures and tempering conditions are presented here. The hyperbolic tangent (solid) and manual (dotted) fits as described in section 3.6.1 are also included. It should be noted that the data here are displayed on a testing temperature scale of -300 to 300 °C, while curves within the thesis are displayed on a temperature scale of -200 to 200 °C. Curves were displayed in the thesis in such a manner as to only represent the testing temperature scale for which physical data had been collected. The testing temperature scale employed in this appendix serves the purpose to represent the full shape of the fit curve.

Figure J.1 Impact energy (J) as a function of testing temperature (°C) for a tempering time of 1 s and tempering temperatures of 305, 366, 427, 489, and 550°C.
Figure J.2  Impact energy (J) as a function of testing temperature (°C) for a tempering time of 10 s and tempering temperatures of 271, 329, 386, 444, and 501°C.

Figure J.3  Impact energy (J) as a function of testing temperature (°C) for a tempering time of 100 s and tempering temperatures of 241, 295, 350, 404, and 458°C.
Figure J.4  Impact energy (J) as a function of testing temperature (°C) for a tempering time of 3600 s and tempering temperatures of 200, 250, 300, 350, and 400°C.
APPENDIX K

% SHEAR LIP ANALYSIS

Images of Charpy fracture surfaces associated with each tempering condition are displayed here. Original images, as well as those including the filled in shear lip area, are displayed.

<table>
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</thead>
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<tr>
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<tr>
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<td>427</td>
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<tr>
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<td>489</td>
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<tr>
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<tr>
<td>RT</td>
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</tr>
<tr>
<td>100</td>
<td></td>
</tr>
<tr>
<td>200</td>
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</tr>
</tbody>
</table>

![Figure K.1 Charpy fracture surfaces corresponding to a tempering time of 1 s and the given tempering temperatures and testing temperatures.](image-url)
Figure K.2 Charpy fracture surfaces corresponding to a tempering time of 1 s and the given tempering temperatures and testing temperatures with included pct. shear lip area shading.
Figure K.3  Charpy fracture surfaces corresponding to a tempering time of 10 s and the given tempering temperatures and testing temperatures.
Figure K.4 Charpy fracture surfaces corresponding to a tempering time of 10 s and the given tempering temperatures and testing temperatures with included pct. shear lip area shading.
Figure K.5  Charpy fracture surfaces corresponding to a tempering time of 100 s and the given tempering temperatures and testing temperatures.
Figure K.6  Charpy fracture surfaces corresponding to a tempering time of 100 s and the given tempering temperatures and testing temperatures with included pct. shear lip area shading.
Figure K.7  Charpy fracture surfaces corresponding to a tempering time of 3600 s and the given tempering temperatures and testing temperatures.
Figure K.8 Charpy fracture surfaces corresponding to a tempering time of 3600 s and the given tempering temperatures and testing temperatures with included pct. shear lip area shading.
APPENDIX L

% SHEAR LIP CURVES

Data pertaining to pct. shear lip for a variety of testing temperatures and tempering conditions are presented here. The hyperbolic tangent (solid) and manual (dotted) fits as described in section 3.6.1 are also included. It should be noted that the data here are displayed on a testing temperature scale of -300 to 300 °C, while curves within the thesis are displayed on a temperature scale of -200 to 200 °C. Curves were displayed in the thesis in such a manner as to only represent the testing temperature scale for which physical data had been collected. The testing temperature scale employed in this appendix serves the purpose to represent the full shape of the fit curve.

Figure L.1 Pct. shear lip as a function of testing temperature (°C) for a tempering time of 1 s and tempering temperatures of 305, 366, 427, 489, and 550°C.
Figure L.2 Pct. shear lip as a function of testing temperature (°C) for a tempering time of 10 s and tempering temperatures of 271, 329, 386, 444, and 501°C.

Figure L.3 Pct. shear lip as a function of testing temperature (°C) for a tempering time of 100 s and tempering temperatures of 241, 295, 350, 404, and 458°C.
Figure L.3 Pct. shear lip as a function of testing temperature (°C) for a tempering time of 100 s and tempering temperatures of 241, 295, 350, 404, and 458°C.

Figure L.4 Pct. shear lip as a function of testing temperature (°C) for a tempering time of 3600 s and tempering temperatures of 200, 250, 300, 350, and 400°C.
APPENDIX M
SEM FRACTURE SURFACE MICROGRAPHS

Displayed are SEM micrographs associated with one position along the Charpy specimen fracture surface (see section 3.8). These micrographs, along with micrographs associated with position 2 along the Charpy fracture surface, were employed to determine brittle point fraction for room temperature testing and to inform the manual fits associated with DBTT and pct. shear curves. Room temperature conditions corresponding to a tempering parameter of 11,000 and 12,000 were chosen to be investigated as these tempering parameters fall within the regime associated with TME. All other time-temperature combinations with a displayed micrograph were investigated for the purpose of informing manual fit curves.

![Image of SEM micrographs](image_url)

Figure M.1 Scanning electron microscopy images of Charpy fracture surfaces corresponding to a tempering time of 1 s and the indicated tempering temperatures and testing temperatures.
Figure M.2 Scanning electron microscopy images of Charpy fracture surfaces corresponding to a tempering time of 10 s and the indicated tempering temperatures and testing temperatures.
Figure M.3 Scanning electron microscopy images of Charpy fracture surfaces corresponding to a tempering time of 100 s and the indicated tempering temperatures and testing temperatures.
Figure M.4  Scanning electron microscopy images of Charpy fracture surfaces corresponding to a tempering time of 3600 s and the indicated tempering temperatures and testing temperatures.