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of a High Toughness Secondary Hardening Steel

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THE EFFECT OF NICKEL CONTENT ON THE MECHANICAL PROPERTIES AND MICROSTRUCTURE OF A HIGH TOUGHNESS SECONDARY HARDENING STEEL

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ABSTRACT

Certain structural applications require materials to possess both high strength and high toughness, two properties which can often be inversely related with one increasing at the expense of the other. Currently, only two classes of steels exist that fulfill both of these application-critical criteria – maraging steels and some cobaltcontaining secondary hardening steels. Unfortunately, these alloys are expensive due to their high cobalt and nickel contents. It is thought that in these alloys nickel offsets the detrimental effects cobalt can have on the ductile-to-brittle transformation and that by removing cobalt, an inexpensive steel alternative with comparable mechanical properties to the currently available alloys could be developed.

This research examines the effect of nickel additions to a base secondary hardening steel on mechanical properties and microstructure. The work was divided into separate studies in which five experimental alloys with differing nickel amounts were examined in order to determine the effect of nickel on the strength, ductile-to-brittle transition temperature (DBTT), and room temperature fracture toughness.

In the first study, the effect of nickel on strength was investigated. Increasing nickel content generally increased strength, although the effect of nickel on yield strength and ultimate tensile strength was highly dependent on the quench rate from the austenitizing temperature. Results indicate that fine precipitates of VC and Mo_2C contribute to the strength of these alloys.

The second study looked at the effect of nickel on the DBTT. Test specimens were heat treated uniformly and then Charpy impact energies were determined for five test temperatures. The DBTT decreased approximately 200°C when nickel content was increased from 0 to 5 and 6 wt.%. Heat treatment did not have a significant effect on the DBTT. Results of testing for the nickel-free alloys suggest that rare-earth inclusions are slightly more effective in promoting quasi-cleavage than calcium or aluminum oxide inclusions. The DBTT was primarily controlled by nickel content, as the effects of prior austenite grain size and retained austenite content were negligible.

In the third and last study, the effect of nickel on room temperature toughness was analyzed. Fracture toughness increased with increasing nickel content and tempering temperature. The experimental alloys with zero nickel additions had unexpectedly low toughness compared to previous work in heats with nearly identical composition. This was determined to be the result of the large inclusions in these steels which promote quasi-cleavage fracture in the absence of nickel. In addition, the difference in toughness between the two experimental base heats could be due to the low coefficient of thermal expansion of rare-earth inclusions, which could increase tensile circumferential stresses that promote quasi-cleavage. Examination of K_{IC} fracture surfaces revealed no correlation between average area fraction of secondary voids and fracture toughness.

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1. INTRODUCTION

For structural materials, two of the main criteria for material selection are strength and toughness. Unfortunately, these two properties can often be inversely related, with one increasing at the expense of the other. Currently, there exist only two classes of steels that possess both high strength and toughness: certain types of maraging steels and some cobalt-containing secondary hardening steels, like Carpenter AerMet[®] 100 Alloy (U.S. Patents: 5,087,415 and 5,268,044).

These high strength, high toughness alloys can contain anywhere from 8-14 wt. % cobalt and 11-18 wt.% nickel. However, cobalt is quite expensive due to its limited availability as a natural resource. An estimated 50% of the world's cobalt exists within the boundaries of the war-torn Democratic Republic of the Congo and must be produced from byproducts of copper and nickel mining¹. Additionally, the need for cobalt in a variety of markets, such as solar panels, batteries, and turbine blades in energy industries, further increases its demand and cost. Consequently, there has been a strong economic driving force to optimize the cost and production of these high strength, high toughness steels by reducing cobalt content.

Cobalt is primarily used as a strengthening agent in the two classes of available ultra-high strength, high toughness steels. However, cobalt has been shown to raise the ductile-to-brittle transition temperature (DBTT), which can reduce room temperature toughness. Conversely, research has shown that nickel has the opposite effect on the DBTT. As both maraging steels and high toughness cobalt-containing secondary hardening steels contain large amounts of cobalt and nickel, it is hypothesized that nickel offsets the detrimental effects of cobalt on the DBTT. Therefore, it could be possible to formulate a new alloy system, one containing zero cobalt and significantly less nickel, that would still exhibit both high strength and high toughness at room temperature and have a reasonably low DBTT.

The purpose of this work focsues on the development of new steels which have high strength and toughness but which contain no cobalt and a maximum of 5-6 wt. % nickel. This research concentrates specifically on mechanical properties and microstructure that result from the eliminating cobalt and varying the nickel content of a base secondary hardening steel. In the following chapters of this document, necessary background information about strength, DBTT, toughness, and ductile fracture and the factors that influence these properties are given. Previous work on the development of cobalt-free steels and the preliminary research that served as a basis for the experimental alloys used in this thesis project are reviewed, followed by a discussion of the effects of composition on the mechanical behavior and microstructure of these new cobalt free, reduced nickel ultra-high strength steels. Finally, the industrial implications of this research and recommendations for future work are addressed.

2. TECHNICAL BACKGROUND

2.1 Microstructure and Heat Treatment of Martensitic Steels

A martensitic microstructure is obtained by first austenitizing, i.e. heating to a temperature in which austenite is stable. Then, the steel is cooled, or "quenched," at a sufficiently quick rate such that austenite is transformed to martensite. This as-quenched structure is then "tempered" by holding for a period of time in the temperature range of 200°C-750°C to achieve the final microstructure. This microstructure is nominally martensitic and usually contains some amount of austenite. In addition, these steels contain different types of second phase particles.

All steels contain inclusions which are typically sulfide, oxide, and nitride particles. There can also be fine carbides that are inherited from the austenitizing temperature, especially when the steels contain strong carbide forming elements. Additional second phase particles can be precipitated during the tempering process.

2.1.1 Phases of Interest

The martensite in these steels can be either body-centered cubic (BCC) or body-centered tetragonal (BCT), depending on the carbon left in solid solution. There are two martensite morphologies: lath or plate². Lath martensite has been shown to have a hierarchical microstructure: packets, blocks, sub-blocks, and laths³. The prior austenite grain is divided up into packets made up of units on the same habit plane called blocks. Laths within blocks have a similar crystal orientation (**Figure 2.1**) and are grouped into sub-blocks which correspond to a single variant of the Kurdjumov-Sachs orientation relationship with austenite.

The type of martensite is strongly influenced by carbon content. Generally, when low alloy steels have carbon contents less than 0.6 wt.%, the matrix will be of the lath martensite type. For steels with carbon contents greater than 1.0 wt.%, the martensite will be plate-like. For carbon contents between 0.6-1.0 wt.%, the martensite type will be a mixture of lath and plate. In steels of interest here, the martensite will be of the lath type (**Figure 2.2a**).



Figure 2.1: Schematic illustration of lath martensite.³



Figure 2.2: (a) Bright field transmission electron micrograph depicting lath martensite in a secondary hardening steel of composition Fe-4Mo-0.2C wt% and (b) the corresponding dark field transmission electron micrograph of inter-lath austenite.⁴

Austenite is also present in martensitic steels. Austenite can either remain in the matrix after cooling from the austenitizing temperature (retained austenite) or be formed from martensite during high temperature annealing in later heat treatments (reverted austenite).

The likelihood that retained austenite will be present in the microstructure after heating to the austenitizing temperature and subsequent quenching is dependent on the temperature at which the martensitic transformations begins on cooling, the martensite start temperature (M_s). If an alloy has a sufficiently low M_s, quenching will result in an incomplete conversion of the austenite to martensite, resulting in the presence of retained austenite in the microstructure, usually as films between martensitic laths (Figure 2.1b)⁵. Retained austenite has also been observed outlining martensite packets and on prior austenite grain boundaries. The M_s is strongly affected by the composition of the material. Yeo⁶ examined the effects of a number of alloying additions on the M_s of a Fe-22.5Ni maraging steel. He found that regardless of alloying content, cobalt increased the M_s, while other elements (titanium, vanadium, niobium, and silicon) initially raised the M_s then lowered it as alloying percent increased. Chromium and nickel were shown to lower the M_s, and aluminum had no effect. Separate studies have shown that in many other steels, cobalt can lower the M_s⁷. In general, the degree to which alloying elements influence the M_s, will depend on the composition of the steel to which the alloying elements are made.

2.1.2 Common Heat Treatment Techniques

Steels are rarely used in their as-quenched condition and normally undergo some heat treatment after quenching from the austenitizing temperature. There are a number of post-austenitizing treatments used in industry that vary based on steel composition and desired properties. The most commonly used post-austenitizing treatment is to heat the asquenched material to a temperature in the range of 200°C-750°C and hold at this temperature for a few hours. This processing is called tempering if the steel contains carbon or aging if the steel does not contain carbon.

Tempering – Tempering occurs after the quench from the austenitizing temperature and typically involves holding the as-quenched material for some period of time (1-5 hours) at a temperature between 200°C and 750°C. During the tempering process, ductility is recovered and residual stresses caused by the martensitic transformation can be relieved. In martensitic steels, tempering involves the segregation of carbon to lattice defects, precipitation of carbides, decomposition of retained austenite, and the recovery and recrystallization of the martensitic structure. Low alloy steels and secondary hardening steels undergo a tempering step during heat treatment^{5,8}.

Aging – Other steels, such as the maraging steels, achieve the desired mechanical properties through aging after austenitizing and quenching. During aging fine intermetallic particles are precipitated, resulting in precipitation strengthening⁹.

2.2 Toughness and Fracture Behavior

Toughness is the term used to describe the ability of a material to resist fracture due to monotonic loading in the presence of a defect of some type. It can be considered the energy to break a specimen containing a notch or crack or the energy per unit area of crack extension required to extend a sharp crack by fracture. Fracture modes can be classified as ductile or brittle. There are two types of brittle fracture: intergranular fracture and cleavage/quasi-cleavage. In brittle intergranular fracture, a fracture path is formed along grain boundaries that have become embrittled due to the segregation of certain impurities to those boundaries. Cleavage fracture occurs transgranularly by the breaking of bonds across low index planes, known as cleavage planes, which are {100} types planes in BCC metals¹⁰⁻¹². Fracture in martensitic steels can also occur through quasi-cleavage, which has mixed brittle and ductile characteristics. The roughly planar facets in quasi-cleavage fracture are not formed along the [100] planes observed in BCC metals and link together through ductile tearing, creating a fracture path¹². In some cases, it is believed that the fracture path during quasi-cleavage is along martensitic lath boundaries, a fracture mode known as inter-lath quasi-cleavage. Ductile fracture, discussed more extensively in Section 2.2.1, results from the growth and coalescence of voids nucleated at inclusions and other second phase particles within the material. Generally, materials that exhibit high toughness will have a microstructure that allows for considerable plastic deformation under stress and will fail by ductile fracture.

2.2.1 Ductile Fracture

In ductile fracture, voids that either pre-exist in the material or, more typically, which are nucleated during deformation can create a continuous fracture path. Ductile fracture can be divided into three major stages:

- 1. Void nucleation
- 2. Void growth
- 3. Void coalescence

It is important to note that ductile fracture is more complicated than three non-overlapping consecutive steps, and definitive delineation between stages of the ductile fracture process is difficult. Nevertheless, each stage of the fracture process is discussed as a separate entity below. *Void Nucleation* – In materials whose fracture mode is ductile, voids will initiate at certain microstructural features within the matrix. For most metals, second phase particles act as void nucleation sites. In steels, these sites are inclusion particles such as oxides, sulfides, and/or nitrides that formed during processing. However, some metallic systems have been shown experimentally to nucleate voids at features other than inclusions¹³⁻¹⁵. For example, certain titanium alloys can form voids at α - β interfaces and at slip bands¹⁴, while voids in oxygen free high conductivity (OFHC) copper can nucleate at grain boundaries¹⁵.

Void nucleation at second phase particles can occur in two ways: decohesion of inclusion particles from the matrix¹⁶ or by particle fracture^{17,18}. The mechanism of void nucleation is dependent on particle size and morphology, as well as the cohesive bond between the particle and the matrix. Research suggests that void nucleation initiated by particle fracture will be favored over decohesion of particles from the matrix when the particle size and/or the strength of the interfacial bond is increased and particles shapes are non-equiaxed^{19,20}. An inclusion population's ability to resist void nucleation has a significant impact on the upper shelf fracture toughness of steels, a subject that will be discussed further in Section 2.3.1.3.

Void Growth – Once voids have been initiated, the way in which they will expand under continued stress is determined by material properties and test conditions. Plastic deformation, which is required for void growth, is believed to occur through dislocation motion. However, the models used to predict void growth are not based on dislocation mechanisms. Rather, these models are rooted in continuum mechanics, which considers the bulk material rather than individual dislocations. Of the continuum models proposed for void growth, the most significant are those of McClintock and Rice and Tracey. McClintock^{21,22} developed equations that described the growth of voids of different geometries in materials that behaved as linearly hardening, non-hardening, or a hardening behavior between those two extremes. For the growth of ellipsoidal holes, he estimated:

$$\frac{1}{R}\frac{dR}{d\bar{\varepsilon}} = \frac{\alpha}{1-n} \left[(1-n)\frac{\sigma_m}{\tau_0} \right]$$

where R is the mean radius of three semiaxes of the void, α is a constant on the order of unity, $\bar{\epsilon}$ is the equivalent plastic strain, n is the work hardening coefficient, σ_m is the mean stress, and τ_0 is yield stress in shear.

McClintock's work suggested that for a constant stress state, void growth decreases as the work hardening coefficient of a material increases. Perra²³, evaluating McClintock's model, found that McClintock's equations underestimated the extent of void growth. Perra also confirmed the significance of stress triaxiality in void growth that McClintock's equations had predicted.

Rice and Tracey's work²⁴ regarded void growth in a rigid, perfectly plastically deforming material. They described the growth of an individual void by the equation:

$$\frac{dR}{d\bar{\varepsilon}R} = 0.283 exp \left[+ \frac{\sqrt{3}}{2} \frac{\sigma_m}{\tau_0} \right]$$

where R is the average void radius, $\bar{\varepsilon}$ is the effective strain, σ_m is the mean stress, and τ_0 is yield stress in shear. Tracey's extension of his work with Rice agreed with McClintock's equations concerning the work hardening behavior²⁵. Further, he found that at a constant stress state and work hardening coefficient, the extent of void growth increased with the amount of strain.

The continuum models generally predict that for an isolated void, the rate of void growth will increase with increasing void size and decrease with increasing work hardening and the rate of void growth increases exponentially as a function of the ratio of the mean stress to the effective or equivalent stress. While qualitatively meaningful, these models generally underpredict void growth seen experimentally because they fail to fully account for void-void interactions. Like void nucleation resistance, void growth affects fracture toughness; more detail on the effect of void growth on fracture behavior is given in Section 2.3.2.

Void Coalescence – In void coalescence, the last stage of ductile fracture, growing voids link together and form a path through which actual fracture can proceed. There are two processes by which void coalescence can occur: direct void impingement or void sheet coalescence. Experimental evidence suggests that void coalescence is generally rapid and occurs over a small strain interval²⁶.

For void impingement, only one type of second phase particles act as sites for void nucleation during the fracture process. These voids then grow until they impinge on each other and coalesce. The two mechanisms that have been proposed for void impingement are (1) the necking down of ligaments separating voids, resulting in a fracture surface with voids of relatively uniform size and spacing²⁷ (**Figure 2.3a**) and (2) a slipping off process that occurs in the fracture of single crystals²⁸. Direct void impingement has been observed in a variety of metallic alloys, including stainless²⁹ and maraging steels³⁰.

Unlike coalescence by direct void impingement, void sheet coalescence occurs when there is more than one population of second phase particles that act as void nucleation sites. Nucleation of voids will typically initiate first at the particles with the weakest bonding to the matrix (primary particles). Then, later in the fracture process and after

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some amount of growth of the voids formed at primary particles (primary voids), void nucleation will activate at a second population of particles (secondary particles). These particles are typically smaller than the primary initiating particles and are more strongly bonded to the matrix, thus requiring higher strains to be reached before acting as void nucleation sites³⁰. In steels, primary particles are typically inclusions, while secondary particles are usually fine carbides that were undissolved during the austenitizing process or carbides that precipitated during later heat treatments such as tempering. The coalescence of the primary voids is caused by the growth and coalescence of the voids formed at the secondary particles, secondary voids, in a process called void sheet coalescence^{30.31} (Figure 2.4). Fracture surfaces typical of void sheet coalescence are characterized by large dimples separated by regions of dimples that are much smaller in scale (Figure 2.3b). As in primary void nucleation, secondary voids can activate at microstructural features other than inclusions or secondary particles. Such sites observed experimentally are slip bands³² and grain boundaries³³.



Figure 2.3: Fracture surface exhibiting (a) direct void impingement in a Vitallium alloy³⁴ and (b) void sheet coalescence in a low carbon steel³⁵.



Figure 2.4: Schematic of void sheet coalescence during ductile fracture.³⁶

2.2.2 Ductile-to-Brittle Transition

Materials having BCC, BCT, or hexagonal close packed (HCP) crystal structures experience a transition in fracture behavior that is temperature dependent. At higher temperatures, these materials can have high toughness and fail by ductile fracture. At lower temperatures, the same materials will exhibit brittle fracture characteristics and consequently, have much lower toughness values. The temperature at which this transition occurs is known as the ductile-to-brittle transition temperature (DBTT). Usually, the DBTT is determined for steels by plotting the Charpy impact energy (CVN) as a function of test temperature, as shown in **Figure 2.5**. The region of high energy exhibits ductile fracture and is known as the upper shelf, whereas the region of low energy exhibits brittle fracture and is known as the lower shelf. The transition from ductile to brittle failure modes is also evidenced on the fracture surfaces of these test specimens, with surface features exhibiting dimples and voids characteristic of ductile fracture at temperatures above the DBTT, brittle fracture at temperatures below, and a mix of ductile and brittle through the transition temperature range. Normally in steels, brittle fractures would be cleavage or quasicleavage, although brittle intergranular fractures is sometimes observed.



Figure 2.5: Representation of determination of the ductile-to-brittle transition by measuring Charpy impact energy as a function of test temperature³⁷.

The DBTT is highly dependent on the microstructure and composition of the steel. It is also affected by strain rate and notch severity. In general, it is desired that the DBTT be below the lowest expected service temperature. Thus, the DBTT is an important parameter to be considered in the development of a new structural steel.

2.2.3 Assessing Toughness

The two most common ways of assessing toughness are the plane strain fracture toughness (K_{IC}) and Charpy impact energy. Although these two tests both provide information about the toughness of a material, they differ in terms of strain rate, the nature of the defect used to promote fracture, and the actual quantity being measured.

The stress intensity factor, K, at fracture is the most common way that fracture toughness is measured. K can be evaluated using one of three different fracture modes: tensile (Mode I), in-plane shear (Mode II), and anti-shear (Mode III) (**Figure 2.6**). These modes are denoted with a Roman numeral subscript, e.g. K_{II} . In Mode I, the crack surfaces move directly apart (*tensile opening*). In Mode II, the crack surfaces slide in shear over one another in a direction perpendicular to the leading edge of the crack (*sliding*). In Mode III, the crack surfaces move relative to one another and parallel to the edge of the crack (*tearing*). Mode I is the most commonly used fracture mode for engineering design and fracture toughness measurements.



Figure 2.6: Three loading modes of cracked specimens: (A) Mode I: tensile (opening); (B) Mode II: inplane (shearing); and (C) Mode III: anti-plane shearing (tearing)³⁸.

In a fracture toughness test, a sample with a sharp pre-initiated crack is loaded at a steady rate until fracture. The resulting data can be used to calculate the highest stress intensity at which the crack will not propagate. For Mode I fracture, this critical value is known as K_{IC} . K_{IC} can be determined using the following equation:

$$K_{IC} = \sigma_C \sqrt{\pi a \beta}$$

where σ_c is the applied stress at fracture, *a* is the crack length, and β is a constant based on the geometry of the sample¹⁰. The stress intensity

factor can vary with crack size and the size and shape of the test specimen.

The Charpy impact test is another common method used to assess fracture toughness. In Charpy testing, a notched sample is loaded onto a stage and struck and broken with a weighted pendulum hammer. The Charpy impact energy, C_v , is the energy absorbed by the test specimen during the fracture process. Although the Charpy impact energy is not a measure of a material's fracture toughness, there is to some degree a correlation between K_{IC} and Charpy impact energy. However, there are some instances in which altering heat treatment can raise the K_{IC} but lower the impact energy. One such example is the effect of raising austenitizing temperature for a low alloy steel as shown by Ritchie³⁹. Charpy testing is widely used due to its advantages over fracture toughness testing – specimens are smaller and less expensive than those of K_{IC} fracture toughness tests and the test can be performed more quickly.

While Charpy impact testing cannot be used to accurately predict K_{IC} fracture toughness, work to establish a relationship between yield strength (σ_y), Charpy impact energy, and K_{IC} fracture toughness has resulted in several equations which follow the form:

$$\left(\frac{K_{IC}(T)}{\sigma_{y}(T)}\right)^{2} = \alpha \left(\frac{C_{v}(T)}{\sigma_{y}(T)}\right) - \beta$$

where K_{IC} , C_v , and σ_y are all functions of temperature and α and β are constants that vary with steel type⁴⁰⁻⁴³.

The Rolfe-Novak-Barsom^{40,41} correlation can be used to estimate upper shelf K_{IC} fracture toughness of steels with a yield strength in the range of 760-1700 MPa:

$$\left(\frac{K_{IC}}{\sigma_y}\right)^2 = 5\left(\frac{C_v}{\sigma_y}\right) - 0.25$$

Ault et al.⁴² suggested the following empirical equation for an ultra-high strength aircraft steel:

$$\left(\frac{K_{IC}}{\sigma_y}\right)^2 = 1.37 \left(\frac{C_v}{\sigma_y}\right) - 0.045$$

Figure 2.7 illustrates the correlation between fracture toughness and Charpy impact energy for several different alloys.



Figure 2.7: Fracture toughness and Charpy impact energy correlation⁴³.

The K_{IC} fracture toughness as determined using ASTM E399 is based on the linear elastic model for fracture mechanics. This assumes that there is only small scale plastic deformation at the pre-initated crack tip, i.e localized yielding at the crack tip is small comparative to the crack length. Previous revisions of this standard were specific about the dimensions of a K_{IC} specimen in order to ensure that plane strain conditions dominate fracture behavior and the stress state at the crack tip minimizes localized plastic deformation there⁴⁴. A K_{IC} value was considered valid when the following specimen dimensional criteria are met:

$$B, a, (W - a) \ge 2.5 \left(\frac{K_{IC}}{\sigma_y}\right)^2$$
$$0.45W < a_0 < 0.55W$$

where *B* is thickness of the test specimen, *a* is crack size, W is width of the specimen, and a_0 is the initial crack size⁴⁵. The current version of ASTM E399 considers a K_{IC} value to be valid when:

$$W - a \ge 2.5 \left(\frac{K_{IC}}{\sigma_y}\right)^2$$

 $P_{max} \ge 1.1 P_Q$

where P_{max} is maximum force the specimen was able to sustain observed and P_Q is the critical load as defined by the 5% secant method corresponding to the appropriate load-displacement curve (**Figure 2.8**).



Figure 2.8: Types of load-placement curves with P_0 defined⁴⁴.

Due to ASTM E399's constraints on both the dimensions of the test

specimen and the fatigue pre-crack, obtaining a valid K_{IC} value for materials of high toughness and/or low yield strength can frequently be difficult because of large scale plasticity at the crack tip. In these instances, linear elastic mechanics can no longer accurately characterize fracture behavior and the *J*-integral approach can be used to test samples of a smaller size that what would be required for valid K_{IC} testing. Requirements for a valid J_{IC} , the critical value of the *J*integral when fracture initiation occurs, are:

$$B, b_0 \ge 25 \left(\frac{J_{IC}}{\sigma_y}\right)$$

where *B* is thickness of the sample and b_0 is the initial crack ligament. The relationship between K_{IC} and J_{IC} values can be described using the equation:

$$J_{IC} = \frac{K_{IC}^{2}}{E} (1 - \nu^{2})$$

where *E* is the elastic modulus and v is the Poisson's ratio of the material¹⁰.

The crack tip opening displacement can also be used as a measure of fracture initiation toughness. During testing of a sample with a sharp crack, there is a finite amount of stress at the crack tip due to plastic deformation that is occurring, rather than the infinite stress predicted by linear elastic predictions. This plastic deformation also blunts the crack tip – this blunting process can be quantified by the crack tip opening displacement, δ . Fracture will initiate when crack tip blunting stops and δ reaches a critical value, δ_{IC} . δ_{IC} , K_{IC} , and J_{IC} can all be related¹⁰ according to the following:

$$\delta_{IC} = d_n \frac{J_{IC}}{\sigma_0}$$
$$J_{IC} = \frac{K_{IC} (1 - v^2)}{E}$$

where σ_0 is the flow stress and d_n is a function of the ratio σ_0/E and the work hardening exponent *n*.

Another measure of fracture resistance is the tensile ductility obtained from tensile specimens. The best measure of tensile ductility is the true strain to fracture (ε_f) and can be determined by:

$$\varepsilon_f = ln\left(\frac{A_0}{A_f}\right)$$

where A_0 is the initial cross-sectional area and A_f is the smallest crosssectional area of the specimen after failure.

The fracture surfaces of both K_{IC} fracture toughness and Charpy impact tests can be used for fractography. Qualitatively, the degree of toughness can be analyzed from the presence and size of shear lips and the fracture modes observed on the fracture surface, e.g. degree of ductile fracture at primary and secondary particles and extent of primary void growth. Energy dispersive electron spectroscopy can be used to gather information about the chemical composition of voidinitiating particles. Quantitatively, the inclusion size and the dimensions of the voids can be measured using scanning electron microscopy.

2.3 Factors Affecting Fracture Behavior and Upper Shelf Toughness

There are a variety of factors that can influence the fracture behavior and toughness of a steel when the fracture mode is ductile. These changes can be attributed to two main sources: inclusions and finescale microstructure. How each of these two categories affects toughness is detailed in the following sections.

The ease by which microstructural parameters can be characterized depends heavily on the complexity of the microstructure. Quantifying inclusions includes determining composition and morphology and measuring volume fraction (f), average inclusion radius (R_0), which is the average particle radius, and the average three-dimensional nearest neighbor inclusion spacing, X₀:

$$X_0 = 0.89 R_0 f^{-1/3}$$

Characterization of the fine-scale microstructure includes measuring the prior austenite grain size, characterizing the secondary particles inherited from the austenitizing temperature, types of martensite, amount and morphology of retained austenite, and the nature of particles precipitated during tempering or aging. In steels containing carbon, these particles would be inter-lath carbides associated with the decomposition of retained austenite and the carbide precipitated within the laths.

2.3.1 Inclusions

Because inclusions are the primary nucleation sites for voids in steels in the ductile fracture process, they play an important role in determining the fracture toughness of a steel. In steels, both primary inclusions and secondary particles (typically fine carbides) impact fracture toughness. When considering a given population of inclusions, inclusion volume fraction (*f*), spacing (X₀), taken as the average nearest neighbor distance in the volume as suggested by Rice and Johnson⁴⁷, and void nucleation resistance all directly factor into the fracture behavior and toughness of a material. Inclusion Volume Fraction – Volume fraction, f, is the volume of a given set of inclusion particles divided by the total volume of the bulk material. For a fixed particle size, volume fraction can be calculated by:

$$f = \left(\frac{4}{3}\pi \overline{R}^3\right) N_V$$

where \overline{R} is the average particle radius (R₀) and N_V is the number of particles per unit volume⁴⁶.

One of the most significant theoretical models for the role of inclusion volume fraction and spacing on fracture toughness is that of Rice and Johnson⁴⁷. They considered a single void of initial radius, R₀, centered a distance X₀ directly ahead of the initially sharp crack tip and formulated a relationship between the critical crack tip opening displacement at fracture, δ_{IC} , and the quantities R₀ and X₀. It was assumed that fracture has initiated when the dimension of the ligament between the blunted crack tip and growing void reached some critical value; in their model, this critical distance was the vertical void radius. The predictions of the Rice and Johnson model are shown in **Figure 2.9**, in which δ_{IC} is normalized by X₀ and plotted as a function of X₀/R₀. Recall that X₀/R₀ = 0.89f^{-1/3} so that X₀ scales as f^{-1/3}. Their numerical results suggest that δ_{IC} scales with both inclusion spacing (X₀) and volume fraction (*f*) by:

$$\delta_{IC} = X_0 F(f)$$

where F(f) is a function that increases slowly with decreasing volume fraction. In applying these results to real materials, they suggested that the X₀ be taken as the average nearest neighbor spacing in the volume. Then, Figure 2.9 is essentially a plot of δ_{IC}/X_0 as a function of $f^{-1/3}$. Therefore, if X₀ is held constant, δ_{IC} will increase with decreasing inclusion volume fraction and the rate of increase becomes smaller as fdecreases.



Figure 2.9: Predicted crack opening displacement at fracture, from the Rice and Johnson model⁴⁸.

A number of experimental studies that have examined the role of inclusion volume fraction on mechanical properties indicate that a decrease in f will increase the fracture toughness. The work of Argon et al showed that a high local volume fraction of second phase particles enhances interfacial strains that will promote separation of particles from the matrix, i.e. void nucleation, at lower strains than areas with a lower inclusion volume fraction⁴⁸. Data from Cox and Low were similar, with results in support of void nucleation at primary particles occurring at much lower strains in materials with higher inclusion volume fractions³⁰. Speich and Spitzig found that increasing the volume fraction of sulfides resulted in a decrease in the axisymmetric tensile ductility and Charpy impact energy of a 4340 steel that was heat treated to a range of strength levels⁴⁹. Additionally, Dulieu and Gouch⁵⁰ showed that in ultra-high strength steels that failed by ductile fracture, increasing the volume fraction of inclusions decreased the K_{IC} value. Edelson and Baldwin⁵¹ investigated the effect of particle volume fraction on tensile properties and found that tensile ductility as measured by the true strain to fracture decreased with increasing particle volume fraction.
The inclusion volume fraction can be decreased to improve fracture toughness and ductility by increasing the "cleanliness" of steel. One of the easiest ways to do so is by utilizing charge material of a higher purity. Additionally, advances in the steelmaking process have allowed for greater control over inclusion content. Techniques such as vacuum induction melting (VIM), electroslag remelting (ESR), and vacuum arc remelting (VAR) make it possible to achieve inclusion volume fractions small enough to produce ultra-high strength steels with sufficiently high toughness for structural applications. The steels studied in this work are very clean steels with oxygen, nitrogen, and sulfur levels of 10 ppm or less. Inclusion volume fraction should be constant in the heats of steel considered in this work, as the heats were all prepared from the same materials using the same melt practice.

Inclusion Spacing – The fracture toughness of a material is significantly influenced by particle spacing due to the gradients in strain, stress, and stress state ahead of a crack tip. When considering the Rice and Johnson model for ductile fraction, fracture toughness, as measured using δ_{IC} , increases linearly with increasing particle spacing at a constant inclusion volume fraction and fine scale microstructure. However, the Rice and Johnson model fails to account for any effect of microstructural features other than inclusion volume fraction and spacing. Experimental work⁵² shows that indeed for a fixed fine-scale microstructure and constant inclusion volume fraction, δ_{IC} does increase with increasing inclusion spacing until a critical distance is reached. Beyond this point, δ_{IC} becomes independent of X_0 .

In practice, inclusion type can affect inclusion spacing. It is common for small amounts of certain alloying additions such as chromium, manganese, titanium, or niobium to be used in order getter sulfur in the form of metal sulfides. Research indicates that when rare earth elements are used in lieu of these alloying additions, the resulting rare earth inclusions in the form of oxides, sulfides, and/or oxysulfides are more widely spaced than inclusions formed in steels when Cr, Mn, Ti, and Nb are used to getter sulfur^{53,54}. Maloney's work on HY180 steel showed that when inclusion types were changed from manganese sulfides to lanthanum oxysulfides the fracture toughness properties were improved⁵³. Since volume fraction was kept constant in this study, the effect of the rare earth inclusions were concluded to be the result of an increase in inclusion particle spacing.

Void Nucleation Resistance of Inclusions – The void nucleation resistance of inclusions is controlled by certain inclusion characteristics: particle size and morphology, strength of the particle/matrix interface, and residual stresses.

Particle Size and Morphology – Void nucleation will occur first at the larger inclusion particles within a given material, and the strain at which voids will nucleate is inversely related to the average inclusion size in the material. This has been experimentally observed in several types of metal systems besides steels, including copper and aluminum alloys^{55,56}. In steels, size dependent void nucleation has occurred at both inclusions and carbides. Void nucleation models disagree over the role of particle size. Gurland and Plateau⁵⁷ and Ashby⁵⁸ postulated that the critical stress for void nucleation decreases with increasing particle size, while Argon⁴⁸ et al. predicted no effect of particle size and Goods and Brown⁵⁹ suggested that larger particles were actually more resistant to void nucleation. However, experimental evidence does seem to support the theory that void nucleation does occur at lower stresses and/or strains for larger particles.

There is also evidence that particle shape affects void nucleation. Gladman's work⁶⁰ showed that spherical particles are the most

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nucleation resistant, followed by elongated particles, and then particles with a plate-like morphology. Non-equiaxed particles are also more likely than spherical particles to internally fracture and initiate voids¹⁹.

Strength of the Particle-Matrix Interface – The higher the interfacial energy between the particle and the matrix in which it is embedded, the lower the work of adhesion will be. Voids are more likely to nucleate at interfaces where the work of adhesion is low, i.e. areas of high interfacial energy⁵⁸. Therefore, controlling the microstructure in order to decrease interfacial energy and thereby increase the void nucleation stress will result in an increase in toughness in ductile materials.

The chemistry at these interfaces plays a critical role in determining resistance to void nucleation. Certain alloying elements have been experimentally shown to increase the cohesive bond between the particle and the matrix. Fischmeister⁶¹ examined the effect of alloying of bond strength between iron and Al_2O_3 particles and found that additions of chromium or molybdenum to an iron matrix greatly increased ductility. Addition of chromium to an iron-nickel base alloy increased the cohesive bond to such an extent that no voids formed at the Al_2O_3 -matrix interface at 75% cold work deformation. It has also been suggested that chromium could be used to increase the cohesive bond between a ferrite matrix and manganese sulfide particles⁶².

Interfacial energy can also be affected by the segregation of elements to the particle-matrix interface. King and Knott⁶³ observed the segregation of phosphorus and tin to the carbide-matrix interface in a low alloy steel and attributed this event to the resulting temper embrittlement. In this study, a decrease in the reduction in area in tensile testing, Charpy impact energy, and δ_{IC} was determined in these embrittled steels. Hippsley and Druce⁶⁴ measured a reduction in void nucleation strain at carbides in 300M steel and attributed it to the segregation of phosphorus and tin which weakened the carbide-matrix interfaces. Like King and Knott's work, a reduced nucleation strain lowered the Charpy impact energy, as well as the J_{IC} values of 300M. In HY180 steel, when sulfur is gettered as titanium carbosulfide, voids are nucleated at much higher strains (Figure 2.10) and the fracture toughness is nearly twice as high when compared to steels whose inclusions are either manganese sulfides or lanthanum oxysulfides^{54,65}. As in HY180, gettering inclusions as titanium carbosulfides increased both nucleation strain and fracture toughness of AF1410 steel over chromium sulfide inclusions in AF1410⁵⁴. While the exact characteristic of titanium carbosulfides that is responsible for increasing toughness in these steels is unknown, it is speculated that the particle-matrix interface has high work of adhesion.



Figure 2.10: Void generation curves for three heats of HY180⁵⁴. Note that void generation begins at much higher strains when sulfides are titanium carbosulfides.

Stress State – The residual stresses normal to the particle-matrix interface caused by differences in thermal contraction must also be considered when evaluating a particle's void nucleation resistance. The stresses normal to the interface are important to void nucleation and can be either tensile or compressive. Brooksbanks and Andrews⁶⁶ found that stress caused by thermal contraction to follow the form:

$$\phi \left[\left(\alpha_1 - \alpha_2 \right) \Delta T \right]$$

where Φ is a function of the matrix and inclusion elastic modulii, and inclusion size and morphology, α_1 and α_2 are the coefficients of thermal expansion for the inclusion and matrix, respectively, and ΔT is the temperature change. The difference in the thermal expansion coefficients is the dominant variable in this equation. If the mean expansion coefficient of the inclusion is larger than the matrix, stresses will be tensile. If the mean expansion coefficient of the inclusion is less than that of the matrix, stresses will be compressive and may increase void nucleation resistance.

Inclusion Type – As previously mentioned, impurities such as sulfur, oxygen, and nitrogen are gettered by different elements added to the melt during the steelmaking process to form inclusions. Such inclusion types include manganese sulfides (MnS), chromium sulfides (CrS), titanium carbosulfides (Ti₂CS), niobium carbosulfides (Nb₂S₂C), and rare earth inclusions in the form of oxides, sulfides, or oxysulfides. These inclusions vary in size, shape, spacing, and void nucleation resistance. Chromium and manganese sulfide particles are small, closely spaced, and not strongly resistant to void nucleation. Similarly, titianium and niobium carbosulfides are small and closely spaced but are very resistant to void nucleation.

As the experimental heats used in this study were modified with rare earth additions, the effect of rare earth elements in ultra-high strength, high toughness steels, such as AF1410 and AerMet 100, is of particular interest. Rare earth oxides, sulfides, and oxysulfides are typically large, widely spaced, and not resistant to void nucleation. Several studies⁶⁷⁻⁶⁹ have shown that rare-earth additions can be used to modify sulfide type so that sulfides are non-deforming globules, which is beneficial during rolling processing. Garrison and Maloney's work⁷⁰ indicated that inclusions formed from rare-earth treated AF1410 resulted in higher toughness values than that of manganese sulfides formed in an AF1410 heat not modified with rare-earth elements. This increase in toughness was attributed to the larger inclusion spacing in the rare earth treated AF1410, based on the predictions of the Rice and Johnson model.

2.3.2 Fine-Scale Microstructure

In addition to the effects of inclusion characteristics on toughness, the fine-scale microstructure of a steel can be critical to fracture behavior. Such factors include the prior austenite grain size, martensite type, fine carbides inherited from the austenitizing temperature, and inter- and intra-lath carbides precipitated during tempering.

Prior Austenite Grain Size – The effect of grain size on strength has been well documented. It would make sense, therefore, that the grain size would affect fracture behavior as well. The upper shelf toughness of steels has been shown to be dependent on austenite grain size, although not for all primary particle spacings. At small particle spacing, toughness is strongly dependent on grain size, increasing with decreasing grain size, whereas the effect of decreasing grain size is not significant at larger particle spacings^{71,72}. A smaller martensite packet size, as determined by prior austenite grain size, as well as finer martensitic lath widths have been shown to increase impact

toughness73.

Martensite Type – The type of martensite, either lath or plate, has been shown to affect fracture toughness. In a study by Yokota and Lai⁷⁴, the toughness of three iron-nickel alloys, with nickel contents of 24, 28, and 32 wt. %, were examined. Their results showed that for a relative constant prior austenite grain size, martensite morphology changed from lath shaped in the 24% Ni alloy to plate-like in the 32% Ni alloy. Additionally, the alloy with the lowest nickel content had the highest yield strength and Charpy impact energy. They concluded that the highly dislocated lath martensite microstructure exhibits better fracture toughness than heavily twinned plate martensite.

Secondary Particles – In steels, the secondary particles are small carbides and nitrides that are inherited from the austenitizing heat treatment and/or that precipitate on tempering. For the latter situation, particles can either precipitate within martensite laths (intra-lath) or on the lath interfaces (inter-lath). Because these particles are capable of nucleating voids later in the fracture process, their volume fraction and resistance to void nucleation can also influence toughness properties. Even if these particles do not act as void nucleation sites, they can still influence fracture properties through their effects on austenite grain/martensite packet size or the flow behavior of the matrix material. One of the most common secondary particles in steels is the cementite carbide, Fe₃C. Unfortunately, there are only a few instances in literature elucidating the role of intra- and inter-lath cementite on the fracture process when the fracture mode is ductile.

Intra-lath Cementite – Intra-lath cementite is typically lath-shaped. Some examples of intra-lath cementite include Widmänstatten cementite and cementite precipitated at martensite twin boundaries. Speich's work⁷⁵ suggested that in HY180 steel, the alloy's high strength and high toughness were the result of precipitation of fine M₂C carbides and the absence of larger embrittling, intra-lath cementite. He argued that because larger particles are less resistant to void nucleation, the large cementite particles were more likely to nucleate voids than the M₂C carbides. Further work by Maloney examining fracture surfaces of HY180 exhibited no evidence of intra-lath cementite as primary particles⁵⁴. However, Handerhan's work⁷⁶ with AF1410 revealed that perhaps intra-lath cementite had acted as void nucleation sites, although the observed particles lacked the characteristic lath shape of intra-lath cementite. It is also possible that the cementite particles seen were not intra-lath carbides that precipitated but were instead inter-lath carbides formed due to decomposition of retained austenite during tempering.

Inter-lath Cementite – Inter-lath cementite forms on either martensite lath boundaries or austenite grain boundaries. Formation on tempering can occur in a few different ways: direct precipitation of carbides at interfaces between martensite laths, precipitation of carbides at the interfaces of intra-lath retained austenite, or as a byproduct of the decomposition of retained austenite. Ayer and Machmeier^{77,78} observed inter-lath films of cementite in AF1410 and AerMet 100 steels and suggested that they could be detrimental to toughness. Cox and Low's paper³⁰ concerning 4340 steel showed cementite on martensitic lath boundaries acted as sites for secondary void nucleation, resulting in an irregular fracture pattern along lath boundaries due to void sheet coalescence.

Carbides Inherited from the Austenitizing Temperature – The other type of secondary particles that can affect toughness properties are undissolved carbides that remain in the microstructure after austenitizing. In HY180, these carbides are typically 20 nm, equiaxed, and take the form MC^{54} . In steels such as AF1410 and AerMet 100, in which the gettering agents are manganese or lanthanum, these carbides are generally larger than those seen in $HY180^{54}$, approximately 50 nm, and take the form $M_{23}C_6$ and M_2C . Because these inherited particles are fine, if they nucleate voids, it will be late in the fracture process and will contribute to void sheet coalescence.

Extent of Void Growth – Void growth continuum models predict that the rate of void growth is a function of void size, the ratio of the mean normal stress to the effective or equivalent stress, and the work hardening coefficient of a material. Experimentally, Aravas and McMeeking⁷⁹ found that the rate of void growth decreased substantially with an increase in the work hardening capacity, i.e. high toughness should be favored by high work hardening capacity. Cox and Low³⁰ investigated void growth rates in a low alloy and maraging steel. Their experimental results suggests that rate of growth of void width is much lower than void growth when stress triaxality was low and that voids nucleated at larger inclusion particles were more likely to have faster growth rates. Additionally, work by Floreen and Hayden⁸⁰ and Psioda⁸¹ suggested that void growth rate increases with matrix strength.

Garrison⁵² has examined the use of the extent of void growth as a measure of local ductility. In his work he studied the sizes of the inclusion-nucleated voids on fracture surfaces by measuring R_{ν} , the radius of the void, and R_I , the radius of the inclusion which nucleated the void. The extent of void growth was taken as R_{ν}/R_I . This quantity was determined for a large number of voids on the fracture surface and the average of these measurements was (R_{ν}/R_I) . Garrison found for many ultra-high strength steels

$$\delta_{IC} \sim X_0 \overline{(R_v/R_I)}$$

where X_0 is the inclusion spacing. It is thought that the extent of void

growth $\overline{(R_v/R_I)}$ is determined primarily by the fine-scale microstructure, e.g. volume fraction of undissolved carbides inherited from the austenitizing temperature⁸².

Blunting Behavior – As previously discussed, the crack tip opening displacement can be used as a measure of fracture initiation toughness. This toughness is dependent on the blunting process at the crack tip. The shape in which the crack tip blunts controls how the strain distribution and rate of void growth ahead of the crack tip change. Possible crack modes that have been observed are smooth, blunting to two corners (square), and blunting to three corners or vertices (sharp) (Figure 2.11). Aravis and McMeeking's work⁷⁹ on the correlation between void growth and the work hardening capacity also suggested that low work hardening and a triaxial stress state would favor nonsmooth blunting and that the rate of void-growth goes to zero directly ahead of non-smoothly blunting cracks. That is, blunting to vertices may be associated with higher levels of toughness than smooth blunting. Garrison⁸³ showed that blunting to vertices appears to be associated with higher toughness than smooth blunting and blunting to vertices is associated with a zig-zag fracture path. In addition, Garrison demonstrated that blunting to vertices is associated with low work hardening, while smooth blunting is associated with high work hardening.

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Figure 2.11: Possible modes of non-smooth crack blunting⁸⁴.

Thus, even though high work hardening rates are believed to slow the rate of void growth, the highest levels of fracture toughness are associated with a low work hardening capacity due to the effect of work hardening behavior on blunting behavior.

2.4 Factors Affecting the Ductile-to-Brittle Transition Temperature

As previously mentioned, martensitic steels are susceptible to a ductileto-brittle transition in fracture behavior. The temperature at which this transition occurs is known as the ductile-to-brittle transition temperature, DBTT. For test temperatures below the DBTT, the fracture mode is primarily brittle and as the test temperature is further decreased the fracture becomes entirely brittle. For test temperatures above the DBTT, the fracture mode is primarily ductile and as the test temperature is further increased, the fracture will become entirely ductile. In the steels considered here, the brittle fracture mode is quasicleavage. Therefore, the DBTT can be thought of as a measure of the steel's resistance to cleavage/quasi-cleavage fracture – the lower the DBTT, the greater the steel's resistance. The DBTT is influenced by the inclusion distributions, the chemical composition of the steel, and the fine scale microstructure.

2.4.1 Effect of Inclusions

When the inclusion particles are relatively fine, they do not promote cleavage or quasi-cleavage fracture or influence the DBTT. However, there is literature implicating large inclusion particles as sites for initiating cleavage or quasi-cleavage fracture. This is the case whether the inclusions fracture^{85,86} (e.g. TiN particles) or debond from the matrix and initiate voids, which provide a stress concentration⁸⁷ (e.g. MnS particles). The heats made for this project were modified by rare-earth additions so inclusions are expected to be rare-earth oxides, sulfides, and oxysulfides. This was done to achieve large and widely spaced inclusions, which favor high toughness when the fracture mode is ductile. However, it is possible that DBTT may increase due to these large and brittle rare-earth inclusion particles.

2.4.2 Alloying Additions

The ductile-to-brittle transition affects steels that have body-centered cubic (BCC) crystal structures, but not face-centered cubic (FCC) ones. Thus, ferritic and martensitic steels, both BCC, will exhibit a ductile-to-brittle transition but FCC steels, e.g. austenitic stainless steel, will not, so long as the austenite does not transform to martensite during deformation.

Within a given system with a stable BCC crystal structure, alloying additions can determine the influence the temperature at which the ductile-to-brittle transition will occur (DBTT). Of particular interest are the effects of nickel and cobalt, the two major alloying elements in ultra-high strength, high toughness steels, on the DBTT. In 1965, Stoloff⁸⁸ showed that cobalt additions significantly increased the DBTT, at roughly 12°C per wt. % cobalt added to the steel (**Figure 2.12**). Adding cobalt had the effect of restricting cell formation and reducing cross-slip in the material, which assisted in cleavage fracture initiation.

Later, Squires and Wilson⁸⁹ found that the DBTT of a base maraging steel increased by 18°C/wt. % cobalt, an effect which was also attributed to cobalt restricting cross-slip.



Figure 2.12: The effect of cobalt on the ductile-to-brittle transition temperature⁸⁸.

Nickel has been shown to have the opposite effect of cobalt, facilitating cross-slip in a steel and lowering the DBTT. Floreen's work⁹⁰ suggested that nickel's effect on cross-slip resulted in a more homogenous distribution of slip throughout the matrix, decreasing the DBTT by 14°C/wt. % nickel (**Figure 2.13**).



Figure 2.13: The effect of nickel on the ductile-to-brittle transition temperature⁸⁹.

2.4.3 Fine Scale Microstructure

There are two major microstructural features that contribute to the ductile-to-brittle transition temperature: grain size and austenite content. Of particular interest is the effect of austenite in the microstructure, either reverted from martensite during the tempering process or retained within the martensitic matrix on cooling from the austenitizing temperature range.

Grain Size – In addition to the effects of grain size on the upper shelf toughness as described in 2.3.2, the grain size can also affect the DBTT, as related by the following derivative of the Hall-Petch relation⁹¹:

$$DBTT = Dln\left(d^{-\frac{1}{2}}\right)$$

where D is a material constant and d is the mean grain size. A fair amount of work supports this correlation. The Fe-Ni alloys examined by

 Kim^{92} were able to obtain excellent toughness at cryogenic temperatures by decreasing the effective grain size by introducing very stable austenite on tempering. Jin^{93} also observed a fairly strong dependence of the DBTT on grain size (8°C/mm^{-1/2}) for an iron-titanium alloy.

Austenite Content – The presence of austenite in BCC metals can have very different effects depending on its distribution and its stability within the microstructure (mechanical and thermal). As previously mentioned, austenite can exist in the microstructure of a martensitic steel in either retained or reverted form.

Reverted Austenite – For some steels during high temperature heat treatments, reversion of metastable martensite to austenite may occur. Austenite formed from such a transformation is known as reverted austenite. This transformation can occur through shear, diffusion, or a combination of the two. The amount of reverted austenite formed is highly dependent on the tempering/aging temperature and steel composition.

Reverted austenite has been shown to have a beneficial effect on the ductility and toughness of steels. Shirazi⁹⁴ suggested that reverted austenite in a Fe-Ni-Mn martensitic steel would increase ductility and toughness. In his work, austenite nucleated at lath and packet boundaries during aging at 600°C. This reverted austenite remained after quenching due to thermal stability provided by saturation of the austenite with nickel and manganese, resulting in a refined microstructure. Cryogenic steels utilize a "QLT" treatment, consisting of direct quenching (Q), intercritical quenching at a relatively low temperature (L), and tempering (T), in order to improve toughness. This increase is due to refining of the effective grain size through the precipitation of thermally stable austenite along prior martensite lath

boundaries95.

Retained Austenite – There are varying effects that retained austenite can have on fracture toughness. First, it can improve toughness by acting as a crack arrestor, according to work by Webster⁹⁶. Mechanistically, this effect seems plausible only if large grains of austenite remain in the matrix. Additionally, the positive effect of retained austenite is more pronounced for microstructures with smaller grain sizes. Since retained austenite for steels examined in this work would most likely be present as inter-lath films, it is unlikely that its presence would have such a beneficial effect. Deformation induced transformation of austenite to martensite, a technique utilized by TRIP (TRansformation Induced Plasticity) steels, can also improve toughness by (1) absorbing energy that would otherwise be used to aid the fracture process⁹⁷ and (2) inhibiting crack growth by creating compressive stresses ahead of the crack trip due to the volume expansion during transformation⁹⁸.

However, not all retained austenite has a positive effect on the fracture toughness of steel. Mechanically unstable retained austenite caused by decomposition of retained austenite during tempering heat treatments has been shown to have a deleterious effect on mechanical properties⁹⁹⁻¹⁰¹. Retained austenite will decompose when tempered at a sufficiently high temperature, which is determined by the composition of the steel. Decomposition of retained austenite begins with the formation of carbides at the interface between the retained austenite and the martensite laths, which lowers the carbon content of the retained austenite so that on quenching from the tempering temperature, some or all of the retained austenite can be transformed to martensite. The retained austenite that remains will have a reduced mechanical stability⁵.

Horn and Ritchie⁹⁵ discovered a direct correlation between the of retained austenite and tempered martensite presence embrittlement (TME). TME is associated with a decrease in room temperature toughness or, more generally, an increase in the ductile-to-brittle transition temperature, on tempering steel in a certain range of tempering temperatures, which are dependent on the composition of the steel. They found the onset of TME in a 0.40 wt. % carbon steel coincided with the tempering range at which inter-lath carbides form and inter-lath austenite become mechanically unstable with respect to deformation. Horn and Ritchie also found the severity of the TME increases as the amount of retained austenite increases. Methods of reducing austenite content cryogenic cooling after quenching and include decreasing austenitizing temperature and time.

In summation, past research suggests that in order to achieve a high toughness steel, both the fine-scale microstructure and inclusion population need to be controlled and manipulated in order to reduce detrimental effects on fracture toughness properties. In this work, the effect of nickel on a base secondary hardening steel's mechanical properties and microstructure were examined in order to optimize strength and fracture toughness.

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3. APPROACH TO DEVELOPMENT OF A NEW HIGH TOUGHNESS STEEL

Of the three types of ultra-high strength martensitic non-stainless steels – low alloy steels of the 300M type, maraging steels, and secondary hardening steels – there are two main reasons secondary hardening steels were chosen as a starting point for the development of an inexpensive high strength, high toughness steel. First, there are already high strength, cobalt-free secondary hardening steels. Second, secondary hardening steels like AerMet 100 have excellence resistance to stress corrosion cracking. This property has been attributed to their (1) fine strengthening carbides that reduce the diffusivity of hydrogen and the crack growth rate during stress corrosion cracking¹⁰² and (2) ability to be heat treated to reduce inter-lath austenite, whose presence has been linked to hydrogen embrittlement and stress corrosion cracking^{103,104}.

3.1 Previous Work

Hot-work die steels are a specific class of secondary hardening steels that are relatively inexpensive and can achieve high hardness¹⁰⁵. However, their low Charpy impact energy and fracture toughness prevent their use in toughness critical applications. Garrison¹⁰⁶ examined the effect of silicon and manganese content on the tempering response and Charpy toughness of one such die steel, H-11 (composition in wt. % is 0.38C-5Cr-1.3Mo-0.5V-1Si-0.5Mn). In this study, three heats were used: H-11, H-11 without manganese, and H-11 without manganese or silicon. He found that while removing manganese has no significant effect on either hardness or toughness, removing silicon significantly improved the Charpy impact energy at high tempering temperatures (**Figure 3.1**). However, the absence of silicon also resulted in a decrease in the peak secondary hardness, necessitating work to find a way increase the hardness without sacrificing the improved toughness.



Figure 3.1: The effect of manganese and silicon of the secondary hardness and the Charpy impact energy of $H-11^{106}$.

Garrison¹⁰⁷ also examined the effects of non-carbide forming elements on the tempering response of a base secondary hardening steel similar to H-11 without silicon or manganese. This base composition, in wt. %, was 0.38C-4.5Cr-2Mo-0.5W-0.5V. Additions (in wt. %) of 2% silicon, 2% aluminum, 4% nickel, 4% cobalt, or 8% cobalt were made to the base steel to determine the effects of these elements on the secondary hardening response as a function of tempering temperature. The results of this study (**Figure 3.2**) showed that 2% Si, 2% Al, and 8% Co had the greatest impact on the secondary hardening peak, while 4% Ni and 4% Co had approximately the same effect, half that of the previous three additions on the base alloy. However, at the tempering temperature that corresponded to peak hardness (550°C), the Charpy impact energies of the 2% Si, 2% Al, and 8% Co were very low. Comparatively, the base alloy, which had the lowest secondary hardness, had the highest Charpy impact energy. The 4 wt% Ni alloy had both high hardness and good Charpy toughness. The base steel with nickel additions of 3 wt. % was used as a starting point for the development of a high strength, high toughness steel.



Figure 3.2: Effects of aluminum, silicon, nickel, and cobalt on a base secondary hardening steel of composition 0.38C-4.5Cr-2Mo-0.5V¹⁰⁷.

3.2 Preliminary Work

An experimental 182 kg heat (ID 011164) was made with the composition of the base steel from the previous study but with an addition of 3 wt. % nickel. Rare-earth elements were also added to this heat to getter oxygen and sulfur impurities. This heat was made by Carpenter Technology Corporation at their Reading, Pennsylvania facility using vacuum induction melting (VIM) followed by vacuum arc remelting (VAR). The mechanical properties of this heat after austenitizing at 1050°C, oil quenching from the austenitizing temperature, refrigerating in liquid nitrogen, and then triple tempering (with liquid nitrogen refrigeration between temper cycles) for the temperatures 525°C, 550°C, and 575°C can be seen in **Table 3.1**.

Table 3.1: Mechanical properties for 01164 (3% Ni) after austenitizing at 1050°C and oil quenching. All specimens were triple tempered and refrigerated in liquid nitrogen after post-austenitizing quenching and between each temper cycle.

Tempering Temperature (°C)	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Reduction in Area (%)	Charpy Impact Energy (J)	K _{IC} Fracture Toughness (MPa√m)
525	1509	1971	55	25.3	109.5
550	1550	1926	48	33.3	125.8
575	1586	1882	65	34.2	145.1

A comparison of mechanical properties of 011164 and current high strength, high toughness steels (**Table 3.2**) indicates that the new experimental steel shows promise. The earlier work by Garrison suggests that adding nickel will increase the strength of the base steel. These results suggest an addition of 3 wt. % Ni is not sufficient to obtain the desired strength levels. As a result, we intend to examine the base steel modified by 5 and 6 wt. % Ni. Thus, we will examine the mechanical behavior of four heats:

- 1. Base steel
- 2. Base steel + 3 wt. % Ni
- 3. Base steel + 5 wt. % Ni
- 4. Base steel + 6 wt. % Ni

Alloy	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Reduction in Area (%)	Charpy Impact Energy (J)	K _{IC} Fracture Toughness (MPa√m)
AerMet 100	1724	1965	65	41	126
C250	1725	1800	50	35	130
011164	1586	1882	65	34.2	145.1

Table 3.2: Comparison of mechanical properties of experimental heat 011164 (3% Ni) and existinghigh strength, high toughness steels.

4. HYPOTHESES AND TECHNICAL APPROACH

The overall objective of this work is to develop a new alloy capable of achieving both high strength and high toughness, with properties comparable to those of maraging steels and specific cobalt-containing secondary hardening steels, such as AF1410 or AerMet 100, and to do so while decreasing costs by reducing expensive alloying additions. Specifically, this research focuses on a base hot work die steel (composition in wt. % 0.38C-4.5Cr-2Mo-0.5W-0.5V) modified with 3, 5, and 6 wt.% Ni in order to study the effect of nickel on three properties: strength, upper shelf Charpy and fracture toughness, and the ductile-to-brittle transition temperature. These specific areas of focus were separated into three studies with distinct hypotheses and corresponding technical approaches to test these hypotheses.

Study I: The Effect of Nickel on Strength – Increasing nickel content will increase the secondary hardening response, and thus, strength.

Greenbank¹⁰⁸ studied the effect of nickel content on the activity coefficient of carbon in Fe-Ni-C austenitic steels at varying nickel contents and temperature by comparing measured carbon concentrations before and after a high temperature soak. He found that the activity coefficient of carbon increased with increasing nickel content and that the effect of nickel was more pronounced at lower temperatures, e.g. 450°C. Based on Greenbank's work, the addition of nickel to the base steel should increase the driving force for precipitation, i.e. nucleation, of strengthening M₂C carbides characteristically observed on tempering secondary hardening steels. A higher nucleation rate should result in finer, more closely spaced carbides, increasing the strength of the alloy. However, increasing nickel content could also increase the amount of retained austenite in the microstructure, which could act to decrease strength.

In order to test our first hypothesis, tensile testing and characterization of the carbides precipitated during tempering are required. Strength will be investigated as a function of nickel content and heat treatment. The three types of carbides that could be present are cementite (Fe₃C), Cr₇C₃, and M₂C, where M could be Cr, Mo, W, and V. The cementite and the Cr₇C₃ should be relatively coarse while the particles of M₂C should be fine needles with a length of about 5 nm. Identification and characterization of the carbides as a function of nickel content (size, number density, and morphology) can be accomplished using dark field imaging mode on a transmission electron microscope (TEM).

Study II: The Effect of Nickel on the Ductile-to-Brittle Transition Temperature – Increasing the nickel content will decrease the ductileto-brittle transition temperature.

Nickel content influences two competing forces that can affect the DBTT. Studies on the effect of nickel on the DBTT of ferritic and martensitic steels indicate that nickel in solid solution will lower the DBTT. Thus, one would expect the addition of 3 wt. % to lower the DBTT and the addition of 5 wt. % to lower the DBTT even further. Conversely, increasing nickel content could also increase the DBTT. Nickel is a known M_s depressant, and if the M_s is sufficiently lowered, the subsequent increase in the amount of austenite retained in the system post-austenization could be increased. This increase could have a significant effect on the DBTT. Due to the high temperatures experienced during tempering in which retained austenite decomposes, the amount of inter-lath carbides and mechanically unstable retained austenite could increase, which act to raise the DBTT.

DBTT testing utilizing Charpy samples and subsequent characterization of specimen fracture surfaces will be used to test the second hypothesis. DBTT will be assessed as a function of nickel content and tempering temperature. In addition, the M_s , prior austenite grain size, and volume percent of retained austenite in the as-quenched and tempered conditions will be measured as a function of nickel content. Retained austenite measurements will be obtained using X-ray diffraction, while grain size can be measured using optical microscopy. M_s calculations will be accomplished using quenching dilatometry.

Study III: The Effect of Nickel on the Fracture Toughness – *Fracture toughness will decrease with increasing nickel content when the fracture mode is ductile.*

To date, the effect of nickel on fracture toughness has been not been thoroughly investigated in ultra-high strength steels. The room temperature fracture toughness is expected to decrease when nickel content is increased, as Charpy impact energy decreased when nickel additions were made to the base steel considered in Garrison's work on the effect of alloying additions on the secondary hardening response. Indeed, his study found that an increase of 4 wt. % nickel to the base steel decreased room temperature Charpy impact energy from 46 J to 36 J. However, as the main objective for this work is the development of an inexpensive, high strength, high toughness alloy, it is possible that even at a nickel level of 4 wt. %, fracture toughness will still be quite high. This study will seek to elucidate the relationship between nickel and fracture toughness.

In these steels, the decomposition of retained austenite will be at high tempering temperatures, coincident with or close to the peak strength due to secondary hardening. The decomposition of the retained austenite will result in carbides precipitating on the interfaces between the martensite laths and remaining retained austenite. As retained austenite will also exist on the packet boundaries and at prior austenite boundaries, carbide precipitation at these locations due to decomposition

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of the austenite is expected. The morphology (sheet or plate-like vs. equiaxed), amount, and size of these are carbides are expected to play a critical role in the upper shelf toughness and DBTT of these steels. When the carbides exist as sheets, it is expected they will promote quasicleavage and act to increase the DBTT. If these carbides become equiaxed, they could nucleate voids. From the standpoint of ductile fracture, fine equiaxed particles are preferred in order to enhance resistance to void nucleation.

It is possible that nickel (and other alloying additions) could influence both the morphology and size of the carbides formed on the decomposition of the retained austenite.

The third hypothesis will be tested by conducting room temperature Charpy and K_{IC} fracture toughness testing as a function of nickel content and tempering temperature. Fracture surfaces and polished cross sections of broken samples will be use to analyze inclusion characteristics (type, size, distribution). Fractography and inclusion analysis will be performed using a scanning electron microscope (SEM). The presence of retained austenite and inter-lath carbides will be investigated using transmission electron microscopy (TEM).

5. MATERIALS AND EXPERIMENTAL METHODOLOGY

5.1 Experimental Alloys

Based on the results obtained from testing of the heat 011164, two more experimental alloys (011301 and 011291) were selected to examine the effect of nickel on the strength, ductile-to-brittle transition temperature (DBTT), and fracture toughness. Later, two additional alloys were made to further explore the effect of nickel on strength and toughness (011481) and the effect on inclusion type on strength, DBTT, and fracture toughness (011480). Compositions of these alloys are listed in **Table 5.1**.

Alloy	С	Cr	Мо	W	V	Ni	
011480	0.37	4.5	2.0	0.5	0.5	0.0	no R.E.
011301	0.37	4.5	2.0	0.5	0.5	0.0	R.E. treated
011164	0.38	4.5	2.0	0.5	0.5	3.0	R.E. treated
011291	0.37	4.5	2.0	0.5	0.5	5.0	R.E. treated
011481	0.37	4.5	2.0	0.5	0.5	6.0	R.E. treated

 $Table \ 5.1: Nominal \ compositions \ and \ heat \ identification \ of \ experimental \ alloys, \ in \ wt. \ \%.$

All experimental alloys were produced by Carpenter Technology Corporation at their Reading, Pennsylvania facility. Alloys were manufactured in 180 kg heats melted using vacuum induction melting (VIM) followed by vacuum arc remelting (VAR). The heats were modified with rare earths in the form of misch metal as a late add during VIM. Heats were homogenized at 1230°C for 16 hours then air cooled before being hot worked (initial forging temperature equal to 1150°C) into flat bars about 40mm thick and 90 mm wide.

5.2 Baseline Heat Treatment

The experimental alloys were subjected to the same baseline heat treatment (**Figure 5.1**). Test specimens first underwent a high temperature hold for 1 hour in a process known as austenization. Austenization occurred in a box furnace with an argon atmosphere. After austenitizing, samples were cooled to room temperature and then refrigerated overnight in liquid nitrogen. Next, samples were removed from the liquid nitrogen and allowed to reach room temperature in air. They were then tempered in a salt pot furnace for 1 hour, water quenched, and then refrigerated in liquid nitrogen overnight. The tempering cycle (temper, quench, refrigeration) was repeated two more times for a total of a triple temper. Three austenitizing temperatures (1025°C, 1050°C, 1075°C), two cooling rates from the austenitizing temperature (oil quenching and air cooling), and three tempering temperatures (525°C, 550°C, 575°C) were employed.



Figure 5.1: Baseline heat treatment for experimental alloys.

5.3 Mechanical Behavior Testing

Smooth axisymmetrical tensile tests, Charpy impact tests, and plane strain (K_{IC}) fracture toughness tests using compact tension specimens were performed. Specimens for these tests were cut from forged bars in an L-T orientation (**Figure 5.2**) and heat treated as oversized blanks before being machined to final dimensions for testing.



Figure 5.2: Schematic representation of L-T specimen orientation with respect to forged bar.

5.3.1 Tensile Testing

Asymmetrical tensile tests were performed using an Instron Series 5500R load frame with standard 6.35 mm diameter round specimens with a 25.4 mm gauge length. The tests were performed at a strain rate of 0.5 mm/min and in accordance with ASTM Standard E8-08¹⁰⁹ and monitored using an Instron 2630-100 Series Static Clip-On extensometer with a gage length of 1". The true strain to fracture, ε_f , of broken tensile specimens was determined by:

$$\varepsilon_f = ln\left(\frac{A_0}{A_f}\right)$$

where A_0 is the initial cross-sectional area and A_f is the smallest crosssectional area of the specimen after failure. Percent reduction in area was calculated by measuring radius at the center of the tensile specimen before and after testing. The tensile properties of the experimental heats were measured at room temperature.

The work hardening exponent, n, was calculated for each of the five experimental alloys using data from tensile tests of specimens austenitized at 1050°C, refrigerated in liquid nitrogen, and triple tempered at 550°C with refrigeration in between tempering cycles. The true stress and true strain up to the maximum load was graphed as a log-log plot. The slope of the line created by this plot was taken to be the work hardening exponent.

5.3.2 Charpy Impact Testing

Standard size Charpy V-notch specimens were tested at room temperature in accordance with ASTM Standard E23-05¹¹⁰ using an Instron impact testing machine (maximum capacity 350 J) at Carnegie Mellon University and a SI-1C Baldwin Impact Tester (maximum capacity 325 J) at Corry Forge Company in Corry, PA. Ductile-to-brittle transition temperature testing using Charpy impact specimens was accomplished by soaking in methanol cooled with liquid nitrogen (sub-room temperature test conditions) or heating in boiling water.

5.3.3 Fracture Toughness Testing

Plane strain fracture toughness testing was conducted using compact specimens with B = 1.5 cm, W = 5.1 cm, and 2H = 6.1 cm. Specimens were machined and tested by Westmoreland Mechanical Testing and Research, Inc. in accordance with ASTM Standard E399-09⁴⁵.

5.4 Microstructural Characterization

Polished cross-sections of specimens for optical microscopy, scanning electron microscopy for inclusion analysis, and X-ray diffraction were mounted and ground sequentially on 240, 300, 400, 600 grit silicon carbide paper. The specimens were then polished using 6 μ m and 1 μ m diamond paste on nylon cloths. A final polish was done using a 0.02 μ m silica suspension on a Buehler MICROCLOTHTM polishing cloth.

5.4.1 Optical Microscopy

Samples of all five experimental alloys austenitized at 1050°C, air cooled, and triple tempered at 575°C were etched to reveal prior austenite grain boundaries. Polished specimens were etched over multiple cycles using a solution of 100 mL water, 7 g picric acid, and 5 g dodecylbenzene salt in an ultrasonic cleaner for an initial submersion of 10 minutes. The specimens were examined using a Zeiss Axio Imager 2 Research Microscope. Grain size was determined using the linear intercept method outlined in ASTM E112-12¹¹¹.

5.4.2 X-Ray Measurement of Retained Austenite

The amount of retained austenite present in the three experimental heats was measured as a function of heat treatment. Measurements were made for the following heat treatment conditions: as-quenched, pre-liquid nitrogen refrigeration; as-quenched, post-liquid nitrogen refrigeration; after one temper, pre-liquid nitrogen refrigeration, after one temper, postliquid nitrogen refrigeration, after two temper cycles, post-liquid nitrogen refrigeration; and after three temper cycles, post-liquid nitrogen refrigeration. Care was taken to use minimal pressure during polishing to minimize mechanical transformation of retained austenite into martensite. Samples were radiated in a Rigaku $\theta/2\theta$ x-ray diffractometer with cobalt radiation at a scan rate of 0.75° /min and setting of 35 kV and 25mA. The integrated intensities under the $(311)_{\gamma}$ and $(220)_{\gamma}$ peaks and the $(211)_{\alpha}$ peak were measured to determine the volume fraction of retained austenite using the following equation¹¹¹:

$$V_{\gamma} = \frac{1.4I_{\gamma}}{I_{\alpha} + 1.4I_{\gamma}}$$

where I_{γ} is the average of the integrated intensity from the $(311)_{\gamma}$ and $(220)_{\gamma}$ planes and I_{α} is the average of the integrated intensity from the $(211)_{\alpha}$ planes.

Scans in which austenite peaks were present were also assessed using the Rietveld Quantitative Analysis, which matches a theoretical line profile to a measured diffraction scan using a non-linear least squares algorithm. The difference between the calculated line profile and the experimental diffraction scan is known as the residual function, M:

$$M = \sum_{i} W_i \left\{ y_i^{obs} - \frac{1}{c} y_i^{calc} \right\}^2$$

where W_i is the statistical weight and c is an overall scale factor such that $y^{calc} = cy^{obs}$. The goal of the Rietveld method is to minimize this residual function by refining various metrics, e.g. lattice parameters, peak width and shape, and preferred orientation¹¹². This technique offers several advantages over the measured integrated intensities approach because it uses the entire diffraction spectrum and is less sensitive to model and experimental errors. For this work, scans were run from 5° to 135° then analyzed using PANalytical X'pert High Score Plus software.

5.4.3 Scanning Electron Microscopy (SEM)

Fractography – Fracture surfaces of broken Charpy impact and K_{IC} specimens were examined using a Philips XL30 FEG and a Quanta 600 FEG scanning SEM. A random series of fractrographs were taken at 500X, 1000X, and 5000X magnification to observe fracture mode and characteristics. Chemistries of visible inclusion particles were obtained using an Oxford INCA/AZtec Electron Dispersive Spectrometry (EDS) System. The area fractions of primary voids, secondary voids, and cleavage/quasi-cleavage features on fracture surfaces were determined by point counting. Using ImageJ software, a grid with an area per point of 0.69 cm² was imposed on each fractograph (a total of 288 points per image). Magnification of all fractographs analyzed according to this method was 1000X. An example image can be seen in Figure 5.3.



Figure 5.3: Example of grid applied to fractographs for point counting analysis.

Fractographs taken at a magnification of 1000X for K_{IC} specimens of 011164, 011291, and 011481 were also examined using ImageJ to determine the average ratio of void radius to inclusion particle radius, R_v/R_I . Ten images for a given heat treatment condition were analyzed for each alloy.

Inclusion Analysis – Inclusion particles in all experimental alloys were studied using a Quanta 600 FEG scanning SEM with a high sensitivity low KV solid state backscatter electron detector (BSED). Halves of fractured Charpy specimens heat treated at 1050°C, air cooled, triple tempered at 550°C, and tested at room temperature were mounted in a KonductoMet thermoset compound and polished. Series of random micrographs at a magnification of 1000X and diameters of inclusions were measured using ImageJ software were taken to determine volume fractions.

 R_0 , the average inclusion radius, was calculated using the harmonic mean H(D):

$$R_0 = \frac{n}{4}H(D)$$
$$H(D) = \frac{N}{\sum_i \frac{1}{d_i}}$$

where N is the number of inclusions, and d_i is the diameter of the ith inclusion⁴⁶.

X₀, the average distance between inclusion particles in the volume was calculated using:

$$X_0 = 0.89 R_0 f^{-1/3}$$

5.4.3 Transmission Electron Microscopy (TEM)

A 200kV FEI Tecnai F-20 Super-Twin and an FEI Titan G2 80-300 scanning transmission electron microscopes equipped with high angle annular dark field (HAADF) detector and EDAX energy dispersive X-ray (EDX) capabilities were used to examine thin foils of specific experimental alloys to investigate strengthening carbides, other precipitates, and retained austenite. Thin foils were prepared from specimens of alloys 011301 and 011291 austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at 550°C with liquid nitrogen refrigeration between each tempering cycle. Slices were cut from these specimens using a slow speed saw and ground on 600 grit silicon carbide paper to approximately 150 µm. The ground slices were then chemically thinned to sub-100 µm using a 5% hydrofluoric acid solution in hydrogen peroxide. 3 mm discs were punched from these foils; these discs were mechanically polished to 70 µm and to remove any residue from the chemical thinning process and electropolished to perforation in a solution of 5% perchloric acid in methanol at -35°C using a voltage of 40 V. Finally, the discs were ion milled using a Gatan Precision Ion Polishing system at 1500 V for 5 minutes.

Simulated patterns used to index the imaged diffraction patterns were created using SingleCrystal software.

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6. RESULTS

6.1 Mechanical Properties

6.1.1 Hardness Measurements

Hardness results for each of the five experimental alloys austenitized at 1050°C, air cooled, and triple tempered at 525°C, 550°C, and 575°C are listed in **Table 6.1**. Generally, average hardness was approximately 54 HRC and similar for all alloys when tempered at 525°C and 550°C. Tempering at 575°C resulted in lower hardness, approximately 51-53 HRC.

Alloy	Temper (°C)	Average Hardness (HRC)		
480 (0Ni, NoRE)		55.6		
301 (0Ni)		55.2		
64 (3Ni)	525	54.3		
291 (5Ni)		54.9		
481 (6Ni)		55.6		
480 (0Ni, NoRE)				
301 (0Ni)		54.7		
64 (3Ni)	550	54.1		
291 (5Ni)		54.1		
481 (6Ni)		54.1		
480 (0Ni, NoRE)				
301 (0Ni)		53.6		
64 (3Ni)	575	53.0		
291 (5Ni)		51.9		
481 (6Ni)		51.1		

Table 6.1: Hardness measurements for all experimental alloys in the air cooled condition.

6.1.2 Tensile Properties

Tensile specimens were tested as a function of austenitizing temperature, quench rate from the austenitizing temperature, and tempering
temperature in order to determine the heat treatment that would yield optimal strength properties. Tensile testing of 011301, 011164, and 011291 was conducted for the following heat treatment conditions:

- Austenization at 1025°C, air cooling, refrigeration in liquid nitrogen, triple tempering at 525°C, 550°C, and 575°C
- Austenization at 1050°C, air cooling, refrigeration in liquid nitrogen, triple tempering at 525°C, 550°C, and 575°C (**Table 6.2**)
- Austenization at 1050°C, oil quenching, refrigeration in liquid nitrogen, triple tempering at 525°C, 550°C, 575°C, and 600°C (Table 6.3)
- Austenization at 1075°C, air cooling, refrigeration in liquid nitrogen, triple tempering at 525°C, 550°C, and 575°C

In addition, 011164 was austenitized at 1050°, oil quenched, refrigerated in liquid nitrogen, and triple tempered at 200°C, 300°C, 400°C, 450°C, 475°C, and 500°C in order to complete a tempering curve for this heat **(Figure 6.1)**.

Tensile testing of experimental alloys 011480 and 011481 was conducted for the following heat treatment condition:

• Austenization at 1050°C, air cooling, refrigeration in liquid nitrogen, triple tempering at 525°C, 550°C, and 575°C (**Table 6.2**)

The effect of a single versus triple temper was also determined for alloys 011291 and 011481 austenitized at 1050°, air cooled, refrigerated in liquid nitrogen, and tempered at 550°C and for 011164 austenitized at 1050°, oil quenched, refrigerated in liquid nitrogen, and tempered at 525°C, 550°C, and 575°C (**Table 6.4**). Single tempers always resulted in lower yield strengths than the triple tempers.

Results of tensile testing for experimental alloys in all heat treatment conditions can be seen in **Appendix Tables A1 – A10**. Estimated error between both yield strengths and ultimate tensile strengths for alloys was approximately 25 MPa, though error for ultimate tensile strength was usually less than that of yield strength.

Peak strength for experimental alloys was observed in air cooled samples austenitized at 1050°C. The effect of nickel content and tempering temperature on tensile properties of specimens austenitized at this temperature and air cooled can be seen in **Table 6.2**. For nickel containing alloys, peak strength was observed after a triple temper of 550°C, while nickel-free alloys exhibited the highest strength on tempering at 525°C. Yield strength was approximately equal for 011291 and 011481. An overall increase of 60 MPa in the air cooled condition was achieved by increasing nickel content from 0 to 5 wt. %.

Alloy	Tempering Temp. (°C)	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Reduction in Area (%)
480 (0Ni, NoRE)		1631	2077	26.2
301 (0Ni)		1637	2056	38.2
64 (3Ni)	525	1580	1991	44.0
291 (5Ni)		1628	2082	48.0
481 (6Ni)		1643	2072	42.7
480 (0Ni, NoRE)		1593	1984	36.0
301 (0Ni)		1573	1953	47.2
64 (3Ni)	550	1606	1976	54.0
291 (5Ni)		1636	2014	56.5
481 (6Ni)		1631	1977	44.9
480 (0Ni, NoRE)		1575	1914	39.8
301 (0Ni)		1510	1846	51.5
64 (3Ni)	575	1566	1871	47.5
291 (5Ni)		1532	1820	43.0
481 (6Ni)		1533	2045	29.2

 Table 6.2: Tensile properties of experimental alloys austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered.

Alloy	Tempering Temp. (°C)	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Reduction in Area (%)
301 (0Ni)		1525	1919	32.7
64 (3Ni)	525	1510	1972	55.0
291 (5Ni)			2045	59.5
301 (0Ni)		1486	1857	65.6
64 (3Ni)	550	1555	1927	47.5
291 (5Ni)		1622	1974	59.9
301 (0Ni)		1527	1850	58.9
64 (3Ni)	575	1582	1879	65.0
291 (5Ni)		1439	1790	57.8
301 (0Ni)		1459	1739	44.8
64 (3Ni)	600	1409	1652	36.5
291 (5Ni)		1422	1559	43.2

Table 6.3: Tensile properties of experimental alloys austenitized at 1050°C, oil quenched, refrigerated in liquid nitrogen, and triple tempered.

Table 6.4: Comparison of mechanical properties for single and triple tempered air cooled 291 and481 specimens and oil quenched 64 specimens.

Alloy	Temper Type	Tempering Temp. (°C)	Yield Strength (MPa)	Ultimate Tensile Strength (MPa)	Reduction in Area (%)	Charpy Impact Energy (J)	K _{IC} Fracture Toughmess (MPa√m)
	Single	525	1458	1979	46.0	25.3	
	Triple	525	1510	1972	55.0	25.2	109.5
64	Single	550	1448	1920	62.0	34.5	
(3Ni)	Triple	550	1555	1927	47.5	33.2	125.8
	Single	575	1517	1903	66.5	29.6	
	Triple	575	1582	1879	65.0	34.2	145.1
291	Single	550	1525	2027	32.3	28.9	99.3
(5Ni)	Triple	550	1636	2014	56.5	26.1	104.9
481	Single	550	1533	2045	25.0	23.5	101.8
(6Ni)	Triple	550	1635	1983	44.9	23.8	113.8



Figure 6.1: Tempering curve for 011164 austenitized at 1050°C, oil quenched, refrigerated in liquid nitrogen, and triple tempered at various temperatures.

Work Hardening Exponent – The work hardening exponents were determined for the five experimental alloys austenitized at 1050° , air cooled, refrigerated in liquid nitrogen, and triple tempered at 550° C and can be seen in **Table 6.5**. These values ranged from 0.14 (011164) to 0.17 (011481) and showed no dependence on nickel content.

Alloy	Work Hardening Exponent, n
480 (0Ni, NoRE)	0.16
301 (0Ni)	0.15
64 (3Ni)	0.14
291 (5Ni)	0.15
481 (6Ni)	0.17

 Table 6.5: Work hardening exponents of experimental alloys austenitized at 1050°C, air cooled,

 refrigerated in liquid nitrogen, and triple tempered at 550°C.

6.1.3 Toughness Properties

Room Temperature Charpy Impact Testing – Similarly to tensile testing, Charpy impact specimens were tested as a function of austenitizing temperature, quench rate from the austenitizing temperature, and tempering temperature in order to determine the heat treatment that would yield optimal toughness properties. For nearly every testing condition listed in 6.1.2 for which a tensile test was performed, corresponding Charpy tests were conducted (**Tables 6.6-6.7**). Results of Charpy impact testing for experimental alloys in all heat treatment conditions can be seen in **Appendix Table A1 – A10**. Estimated error for Charpy values was approximately 2 J.

The effect of nickel content and tempering temperature on Charpy impact energy of specimens air cooled after austenization at 1050°C, the temperature at which peak strength was achieved, can be seen in Table 6.6. Generally, Charpy impact energy increased with increasing nickel content and tempering temperature. The 0% Ni alloys had low Charpy impact energies regardless of tempering temperature. 011164 had peak Charpy impact energy at a tempering temperature of 575°C, while the higher nickel heats 011291 and 011481 had peak Charpy impact energy at a tempering temperature of 550°C.

The effect of temper cycles on Charpy impact toughness on 011164, 011291, and 011481 can be seen in Table 6.4. In general, there is no substantial increase or decrease in impact toughness when the number of temper cycles is increased from a single to a triple temper.

 K_{IC} Fracture Toughness Testing – K_{IC} specimens were austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at 525°C, 550°C, and 575°C. Additionally, specimens of 011164 were prepared by austenitizing at 1050°C, oil quenching, refrigerating in liquid nitrogen, and triple tempering at 525°C, 550°C, and 575°C. Results of K_{IC}

testing are listed in Tables 6.6-6.7. Estimated error for K_{IC} values is approximately 3 MPa \sqrt{m} . As with the Charpy specimens, the 0% Ni alloys had low toughness relative to the nickel containing alloys. However, K_{IC} values increased with increasing tempering temperature, regardless of nickel content; peak toughness was achieved at a tempering temperature of 575°C.

The effect of temper cycles on K_{IC} fracture toughness of experimental heats 011291 and 011481 can be seen in Table 6.4. Although increasing temper cycles had negligible effect on the Charpy impact energy, K_{IC} values increased when tempering cycles were increased from a single to a triple temper. The effect of tempering cycles also increased with increasing nickel content.

A 11 a m	Tempering	Charpy Impact	K _{IC} Fracture
Апоу	Temp. (°C)	Energy (J)	Toughness (MPa√m)
480 (0Ni,		Q /	28.1
NoRE)		0.4	20.1
301 (0Ni)	525	4.1	28.8
64 (3Ni)	525	21.7	97.1
291 (5Ni)		28.2	86.1
481 (6Ni)		25.1	91.6
480 (0Ni,		86	
NoRE)		0.0	
301 (0Ni)	550	5.1	29.4
64 (3Ni)		22.8	108.3
291 (5Ni)		26.9	104.9
481 (6Ni)		23.8	113.8
480 (0Ni,		0.0	22.0
NoRE)		9.9	55.0
301 (0Ni)	575		31.6
64 (3Ni)	575	25.1	119.3
291 (5Ni)		20.7	111.1
481 (6Ni)		21.1	113.0

Table 6.6: Toughness properties of experimental alloys austenitized at 1050°C, air cooled,refrigerated in liquid nitrogen, and triple tempered.

Alloy	Tempering Temp. (°C)	Charpy Impact Energy (J)	K _{IC} Fracture Toughmess (MPa√m)
301 (0Ni)		13.8	
64 (3Ni)	525	22.45	109.5
291 (5Ni)		31.35	
301 (0Ni)		14.95	
64 (3Ni)	550	25.2	125.8
291 (5Ni)		40.9	
301 (0Ni)			
64 (3Ni)	575	33.2	145.05
291 (5Ni)		35.4	
301 (0Ni)			
64 (3Ni)	600	34.15	
291 (5Ni)		27.45	

Table 6.7: Toughness properties of experimental alloys austenitized at 1050°C, oil-quenched,refrigerated in liquid nitrogen, and triple tempered.

Ductile-to-Brittle Transition Temperature Testing – Ductile-to-brittle transition temperature testing was conducted for the five experimental alloys using Charpy impact specimens. These specimens were uniformly heat treated by austenitizing at 1050°C, air cooling, refrigerating in liquid nitrogen, and triple tempering at 525, 550, and 575°C. Testing of specimens were conducted at -194 (liquid nitrogen), -120, -80, -40, 0, 23 (room temperature), and 100°C. Results of testing can be seen in **Figures 6.2-6.4**. Additionally, the DBTT curves for 011291 and 011481 in the single temper condition at 550°C were generated. A comparison of the single versus triple temper conditions on the DBTT can be seen in **Figures 6.5-6.6**.



Test Temperature (°C) Figure 6.2: Results of DBTT testing for experimental alloys austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at 525°C.



Figure 6.3: Results of DBTT testing for experimental alloys austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at 550°C.



Figure 6.4: Results of DBTT testing for experimental alloys austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at 575°C.



Figure 6.5: Results of DBTT testing for 011291 austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and single or triple tempered at 550°C.



Figure 6.6: Results of DBTT testing for 011481 austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and single or triple tempered at 550°C.

6.2 Fractography

6.2.1 Room Temperature Fracture Surfaces

Fracture surfaces of Charpy and K_{IC} specimens tested at room temperature were imaged using an SEM to determine fracture mode and inclusion chemistries and analyze void characteristics in the alloys that failed by ductile fracture.

Imaging of Charpy and K_{IC} fracture surfaces for the 011480 (**Figures 6.7-6.8**) and 011301 (**Figures 6.9-6.10**) 0% Ni alloys corroborated the mechanical behavior data obtained – these heats exhibited primarily quasi-cleavage failure during testing, regardless of heat treatment. As there were no large voids and minimal areas of microvoids, chemical analysis of inclusion particles was not possible.



Figure 6.7: Fracture surfaces of Charpy impact specimens for 011480 austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at (a) 525°C; (b) 550°C, and (c) 575°C.



Figure 6.8: Fracture surfaces of K_{IC} specimens for 011480 austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at (a) 525°C and (b) 575°C. No specimens exist for 550°C as these samples fractured during pre-cracking.



Figure 6.9: Fracture surfaces of Charpy impact specimens for 011301 austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at (a) 525°C; (b) 550°C; and (c) 575°C.



Figure 6.10: Fracture surfaces of K_{IC} specimens for 011301 austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at (a) 525°C; (b) 550°C; and (c) 575°C.

Imaging of Charpy and K_{IC} fracture surfaces for the nickel containing alloys (**Figures 6.11-6.13**) indicated that the primary failure mode of these heat was ductile fracture. Inclusion particle chemistries were obtained using EDS. Inclusions were rare-earth oxides, sulfides, and oxysulfides.



Figure 6.11: Fracture surfaces of Charpy impact (a-c) and K_{IC} (d-f) specimens for 011164 austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at (a/d) 525°C; (b/e) 550°C; and (c/f) 575°C.



Figure 6.12: Fracture surfaces of Charpy impact (a-c) and K_{IC} (d-f) specimens for 011291 austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at (a/d) 525°C; (b/e) 550°C; and (c/f) 575°C.



Figure 6.13: Fracture surfaces of Charpy impact (a-c) and K_{IC} (d-f) specimens for 011481 austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at (a/d) 525°C; (b/e) 550°C; and (c/f) 575°C.

In order to establish a correlation between increasing K_{IC} fracture toughness and increasing nickel content and tempering temperature, the area fraction of primary voids, secondary voids/micro-void regions, and quasi-cleavage regions were determined using the point counting technique described in Section 5.4.3. The results of that study can be seen in **Table 6.8**. The average area fraction of the secondary/microvoid regions was 0.20-0.25 for all three nickel alloys and did not change significantly with tempering temperature.

Alloy	Tempering Temperature (°C)	Primary Voids (%)	Secondary Voids (%)	Quasi- Cleavage (%)
64 (3% Ni)		74	25	0
291 (5% Ni)	525	76	24	0
481 (6% Ni)		80	19	0
64 (3% Ni)		79	20	0
291 (5% Ni)	550	82	18	0
481 (6% Ni)		74	25	1
64 (3% Ni)		78	20	2
291 (5% Ni)	575	76	24	0
481 (6 % Ni)		77	22	1

Table 6.8: Fractography analysis for nickel-containing experimental alloys.

6.2.2 Ductile-to-Brittle Transition Temperature Specimen Fracture Surfaces

Fracture surfaces of broken Charpy specimens used for DBTT testing were imaged using scanning electron microscopy (SEM) to characterize fracture mode. These will be discussed in Section 7.2.

6.3 Inclusion Characterization

Cross-sections of broken Charpy samples for all five alloys were polished and imaged at a magnification of 1000X using an SEM with EDS capabilities to determine inclusion composition, size, morphology, and volume fraction. Radii of inclusion particles were measured using ImageJ software. A minimum of 100 particles were analyzed for each alloy. The results of this study are summarized in **Table 6.9**. In general, the nickel-containing alloys were slightly cleaner than the two base steels. The average inclusion radius was largest in the base steels, though not significantly so. The average nearest neighbor spacing (X_0) between particles increased slightly with increasing nickel content, from 9.4 to 12.8 µm.

	Average Radius (μm)	Volume Fraction	X ₀ (μm)	No. of Particles Analyzed
480 (0% Ni, NoRE)	0.79	1.63E-04	12.9	160
301 (0% Ni)	0.79	2.26E-04	11.5	198
64 (3% Ni)	0.66	2.43E-04	9.4	129
291 (5% Ni)	0.71	1.43E-04	12.1	101
481 (6% Ni)	0.77	1.52E-04	12.8	105

Table 6.9: Inclusion characteristics of experimental steels.

Inclusion particles in the 011164, 011291, and 011481 were equiaxed rare earth oxides, sulfides, and oxysulfides (**Figures 6.14-6.16**). Average radius and volume fraction were comparable for these three alloys.



Figure 6.14: Identification of a rare earth oxy-sulfide in a polished cross-section of a 011164 sample.



Figure 6.15: Identification of a rare earth oxy-sulfide in a polished cross-section of a 011291 sample.



Figure 6.16: Identification of a rare earth oxy-sulfide in a polished cross-section of a 011481 sample.

Inclusion particles in the two base alloys were more complicated. Alloy 011301 contained rare-earth oxides, sulfides, and oxysulfides (Figure 6.17), as well as titanium sulfides (Figure 6.18), calcium oxides (Figure 6.19), and aluminum oxides (Figure 6.20). As titanium was not an alloying element, its presence merited further inspection. Upon investigation, it was determined that the two heats made previous to heat 011301 contained 0.10 wt. % Ti. The concentration of titanium for 011301 was 0.007 wt.% – therefore some contamination did in fact occur during vacuum induction melting. A detailed breakdown of inclusions in this alloy is discussed in Section 7.3. Average inclusion radius and volume fraction is similar to that of the nickel containing alloys.



Figure 6.17: Identification of a rare earth oxide particle in a polished cross-section of a 011301 sample.



Figure 6.18: Identification of a titanium sulfide particle in a polished cross-section of a 011301 sample.



Figure 6.19: Identification of a calcium oxy-sulfide particle in a polished cross-section of a 011301 sample.



Figure 6.20: Identification of an aluminum oxide particle in a polished cross-section of a 011301 sample.

Alloy 011480 was made primarily to assess toughness as a result of changing inclusion type and thus was not rare-earth treated during the melt practice. Inclusions were expected to be small chromium sulfides, as chromium is the only sulfide forming element in the steel. It was felt that the low toughness of heat 011301 was due to the large rare-earth inclusions in the steel in the absence of nickel. However, inclusion analysis revealed primary particles to be large calcium oxides and aluminum oxides (**Figures 6.21-6.22**). The average inclusion radius was larger and the volume fraction of these particles was higher than those in the rare-earth treated alloys but not significantly so.



Figure 6.21: Identification of a calcium oxide particle in a polished cross-section of a 011480 sample.



Average R_v/R_i , the ratio of primary void radius (R_v) to inclusion radius (R_i) values were calculated using SEM micrographs of the fracture surfaces of tested K_{IC} specimens for nickel-containing alloys. The diameters of primary voids and inclusions were measured using ImageJ software. For the purpose of analysis, only voids containing visible single and unbroken inclusion particles were considered. Inclusions whose radius was more than 20% different than average radius measurements were also excluded from the analysis. A summary of these values are listed in **Table 6.10**.

	Temper (°C)	Average R _v /R _i
	525	4.78
64 (3% Ni)	550	6.38
	575	6.42
	525	4.85
291 (5% Ni)	550	6.48
	575	6.31
	525	4.51
481 (6% Ni)	550	7.04
	575	7.21

Table 6.10: Average R_v/R_i values for nickel-containing alloys air cooled from an austenitizing temperature of 1050°C.

6.4 Fine-Scale Microstructure

6.4.1 Prior Austenite Grain Size

Grain size measurements of each alloy were determined using the linear intercept method¹¹¹. For each alloy, grain size was averaged from 10 random images at a magnification of 200X analyzed using 5 lines. Representative images can be seen in **Figure 6.23** and average grain size is reported in **Table 6.11**. Grain size was largest for 011164 (125.8 μ m) and smallest for 011301 and 011480, 67.6 μ m and 65.1 μ m respectively. Grain size decreased from 3% Ni to 6% Ni, although the calculated grain size for 011291, 74.3 μ m, was slightly smaller than that of 011481, 87.0 μ m.

Table 6.11: Prior austenite grain size measureme	ents.
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Alloy	Grain Size (µm)	ASTM Grain Size
480 (0% Ni, NoRE)	65.1	5
301 (0% Ni)	67.6	5
64 (3% Ni)	125.8	3
291 (5% Ni)	74.3	4
481 (6% Ni)	87	4



Figure 6.23: Etched prior austenite grain boundaries in (1) 011480; (b) 011301; (c) 011164; (d) 011291; and (e) 011481.

6.4.2 Martensite Start Temperature

The martensite start temperature, M_s , was measured for 011480, 011301, 011164, and 011291 using dilatometric testing. Measured M_s temperatures for these alloys can be seen in **Table 6.12**.

Allow	Martensite Start
Anoy	Temperature (°C)
480 (0% Ni, NoRE)	340
301 (0% Ni)	320
64 (3% Ni)	260
291 (5% Ni)	200
481 (6% Ni)	190

Table 6.12: Measured martensite start temperatures for experimental alloys.

6.4.3 Retained Austenite

Retained austenite measurements as a function of nickel content and heat treatment were obtained using an x-ray diffractometer (XRD). Retained austenite content was measured successively after each critical step in the heat treating process for 011301, 011164, and 100291. Retained austenite was measured for the following six heat treatments:

- 1. AQ,pLNR (as quenched, pre-liquid nitrogen refrigeration) austenitized at 1050°C and air cooled to room temperature
- AQ,LNR (as quenched, liquid nitrogen refrigeration) austenitized at 1050°C, air cooled to room temperature, then refrigerated in liquid nitrogen
- 1T,pLNR (single temper cycle, pre-liquid nitrogen refrigeration) austenitized at 1050°C, air cooled to room temperature, refrigerated in liquid nitrogen, then given a single temper at 575°C
- 4. 1T,LNR (single temper cycle, liquid nitrogen refrigeration) austenitized at 1050°C, air cooled to room temperature, refrigerated in liquid nitrogen, tempered at 575°C followed by liquid nitrogen refrigeration
- 2T,LNR (double temper cycle, liquid nitrogen refrigeration) same as 1T,LNR but samples were tempered twice at 575°C with liquid nitrogen refrigeration after each temper cycle

6. 3T,LNR (triple temper cycle, liquid nitrogen refrigeration) – same as 1T,LNR but samples were tempered three times at 575°C with liquid nitrogen refrigeration after each temper cycle

Overall, the amount of retained austenite decreased with each step in the heat treatment process and in the triple tempered condition was below the detection limit of the XRD, essentially 0%. This trend can be seen in **Figure 6.24**.



Figure 6.24: Retained austenite content plotted as a function of heat treatment for 011301, 011164, and 011291.

6.4.4 Carbide Characterization

In order to link changes in mechanical properties to corresponding changes in microstructure, TEM thin foils were used to investigate strengthening precipitates. Two alloys were chosen for TEM examination – 011301 (0% Ni with rare earth additions) and 011291 (5% Ni with rare

earth additions). For both 011301 and 011291, the predominant microstructure was martensitic laths approximately 200 nm in width (**Figure 6.25**).

Due to known orientation relationships of strengthening carbides in a BCC matrix, the foil was tilted to a [100] zone axis to reveal faint diffraction spots from these precipitates (**Figure 6.26a**). According to the indexed selected area diffraction pattern (SADP) of the 011301 foil, the observed strengthening precipitates are needle-like cubic VC carbides (**Figure 6.26b**). As their small size makes them hard to detect in bright field (BF) imaging, dark field (DF) images were obtained to determine relative size and morphology (**Figure 6.26d**). The size of multiple VC carbides seen in DF were measured to give an average length of 62 Å.

Strengthening precipitates observed in 011291 were determined to be hexagonal Mo_2C carbides (**Figure 6.27**). In addition to a higher population density, these carbides were much finer than the VC carbides seen in 011301, approximately 9 Å in length. As the diffraction spots indexed were thin, faint streaks (Figure 6.27a), the d-spacings of these indexed hexagonal planes correspond to the radii of the dashed circles in Figure 6.27c.



Figure 6.25: Bright field TEM images showing lath martensite microstructure of (a) 011301 and (b) 011291.



Figure 6.26: (a) [100] Selected area diffraction pattern of 011301 TEM foil. (b) Schematic diffraction pattern for BCC matrix and VC carbide. (c) Bright field image. (d) Dark field image.



Figure 6.27: (a) [111] inverted selected area diffraction pattern of 011291 TEM foil. (b) Theoretical diffraction pattern for large Mo_2C carbide in BCC matrix. (c) Schematic diffraction pattern for BCC matrix and Mo_2C carbide with rings corresponding to $(01\overline{1}0)$ (inner ring) and $(2\overline{1}10)$ (outer ring). (d) Bright field image. (e) Dark field image.

Compositional mapping of selected areas of TEM thin foils was used to further characterize precipitates. Elemental maps can be seen in **Figure 6.28** for 011301 and in **Figures 6.29** for 011291. In 011301, only small vanadium rich carbides can be distinguished. Some of these carbides also show incorporation of titanium (6.29f). The size of these precipitates are similar to those measured from DF TEM images. In 011921, mapping reveals larger intra-lath precipitates rich in chromium, vanadium, and molybdenum approximately 100 nm in length.



Figure 6.28: (a) Mapping of 011301 thin film for elements (b) iron; (c) chromium; (d) molybdenum; (e) vanadium, and (f) titanium.



Figure 6.29: (a) Mapping of 011291 thin film for elements (b) iron; (c) nickel; (d) molybdenum; (e) chromium, and (f) vanadium.

7. DISCUSSION

7.1 Study I: Strength

Heat Treatment Conditions – The majority of mechanical behavior testing conducted and discussed here utilized air cooling from the austenitizing temperature. Although oil quenching after austenitization was investigated to some extent, preparing samples via this method resulted in extensive quench cracking, limiting the number of specimens suitable for testing.

7.1.1 Effect of Heat Treatment

Quench Rate – Slowing the cooling rate from the austenitizing temperature by air cooling instead of oil quenching resulted in increased yield strength and ultimate tensile strength regardless of nickel content (Figures 7.1-7.2). However, the increase in strength seen by decreasing the cooling rate decreased with increasing nickel content. This behavior was unexpected. Slow cooling from the austenitizing temperature is frequently avoided in these alloys to minimize the amount of retained austenite and maximize the toughness at temperatures where peak secondary hardening is obtained and retained austenite decomposition occurs. Certainly, a more thorough investigation of oil quenched tensile properties is needed to elucidate the mechanisms by which the cooling rate from the austenitizing temperature influences strength in this alloy system.



Figure 7.1: Effect of quench rate from the austenitizing temperature on the yield strength of 011301, 011164, and 011291 tested at room temperature. Specimens were austenitized at 1050°C and triple tempered at 550°C.



Figure 7.2: Effect of quench rate from the austenitizing temperature on the ultimate tensile strength of 011301, 011164, and 011291 tested at room temperature. Specimens were austenitized at 1050°C and triple tempered at 550°C.

Tempering Temperature – Although heat treatment conditions for peak strength varied with nickel content, generally peak strength for nickel containing alloys was achieved at 550°C, while peak strength of nickel-free alloys appears to be lower. To date, only one full tempering curve has been completed; this was for 011164 (3% Ni) oil quenched from an austenitizing temperature of 1050°C.

For both of the nickel-free base alloys, the highest yield and ultimate tensile strength was obtained by tempering at 525°C. Strength decreased with increasing tempering temperature. Without a completed tempering curve, it remains uncertain whether 525°C is the temperature at which peak strength is achieved or simply resulted in highest strength for the three tempering temperatures investigated. For 011164, yield strength increased from a tempering temperature of 525°C to 550°C then decreased from 550°C to 575°C, while the ultimate tensile strength decreased with increasing tempering temperature. The results of the tempering curve study of the oil quenched 3% Ni alloy showed that both yield strength and ultimate tensile strength increased from 300°C to peak strength at 575°C before decreasing significantly at a tempering temperatures of 600°C. Therefore, for a nickel content of 3 wt.%, decreasing cooling rate from the austenitizing temperature decreased the tempering temperature at which peak strength is achieved. 011291 (5% Ni) and 011481 (6% Ni) alloys exhibited only slight changes in yield strength when tempered at 525°C and 550°C. However, for both 011291 and 011481, there was a marked decrease in yield strength when the tempering temperature was increased from 550°C to 575°C. Indeed, increasing nickel content seems to increase the drop off in yield strength between peak strength at 550°C to 575°C in the air cooled samples.

Peak strengths for the nickel containing experimental alloys were reached at a much higher tempering temperature than in other commercial secondary hardening steels like AerMet 100 and AF1410, whose peak strengths are obtained between 468°C and 482°C. However, peak tempering temperatures seen in this body of research agree with work previously published by Honeycombe¹⁰⁵, in which peak hardness of vanadium, molybdenum, and tungsten steels were reached at a tempering temperature of 550°C.

Effect of Temper Cycles – The effect of number of tempering cycles on strength properties was also investigated for the nickel containing alloys. For the 3% Ni heat, the mechanical properties of specimens single or triple tempered at 525° C, 550° C, or 575° C and tested at room temperature after being oil quenched from an austenitizing temperature of 1050° C were determined. As with the air cooled samples, peak strength at this nickel content was achieved at 550° C. There was a minimum increase of 50 MPa between the single and triple temper conditions, with the largest increase of 107 MPa seen at 550° C, coincident with peak strength levels. The effect of the number of tempering cycles on strength in 011291 and 011481 alloys for only one tempering temperature (550° C) was examined. Similarly to 011164, the yield strength increased by approximately 100 MPa when the number of tempering cycles was increased from one to three.

The original purpose behind multiple tempering cycles was to reduce the amount of retained austenite, which is potentially detrimental to toughness, using refrigeration cycles. Based on the results of retained austenite studies in Figure 6.24, retained austenite is effectively eliminated after the first temper, before post-tempering even refrigeration, so its presence or lack thereof and/or byproducts of retained austenite decomposition as a result of high tempering temperatures likely has little bearing on strength levels observed. Rather, considering time to peak strength in other secondary hardening steels is much longer, e.g. AerMet 100 and AF 1410 (5 hours)¹¹⁴⁻¹¹⁶, Fe-0.2C-2V (10 hours)¹⁰⁵, and Fe-0.2C-4Mo (25 hours)¹⁰⁵, the increase in yield
strength as a function of tempering cycles is most likely due to an increase in total tempering time, allowing more strengthening carbides to nucleate at peak tempering temperatures.

7.1.2 Effect of Nickel Content

Tensile Properties –For all three tempering temperatures investigated, yield strength and ultimate tensile strength generally increased with increasing nickel content, which supports the initial hypothesis for Study I. Strength was approximately equivalent for a nickel content of 5% and 6%. The highest strength was achieved by increasing nickel content to 5% and triple tempering at 550°C. For samples air cooled from an austenitizing temperature of 1050°C and triple tempered at 550°C, total strength was increased by 63 MPa with a 5% Ni addition.

However, this strength increase, though measurable, was insignificant relative to the magnitude observed, with less than a 5% increase in yield strength overall. This was less than expected based on Garrison's previous study, in which increasing nickel content from 0% to 4.5% increased the hardness by 2.5 HRC, which suggested a strength increase of 150 MPa. A possible explanation for this difference is the heat treatment conditions for the alloys in Garrison's preliminary research, which were oil quenched from the austenitizing temperature. Indeed, examining the results of the oil quenched samples of the experimental alloys shows that increasing nickel content from 0% to 5% resulted in an approximately 135 MPa increase in yield strength, close to what was predicted from Garrison's work.

Work Hardening Exponents – The work hardening exponents for the experimental alloys were relatively constant with respect to nickel content. As such, work hardening can be excluded as a contributing factor to any change in tensile properties. The values calculated also

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correlate to work hardening exponents of alloy systems with similar mechanical properties¹¹⁷.

Prior Austenite Grain Size - While strength increases observed do not follow a standard Hall-Petch relationship with respect to grain size, strength did increase with increasing nickel content and decreasing grain size in the nickel alloys so it cannot be stated with any certainty that grain size did not contribute to changes in tensile properties. However, any effect it might have had would certainly be small given the overall yield strength increase in the air cooled condition. For the contaminated 011301, while the concentration of titanium was small relative to other alloying elements, metals like niobium, titanium, and vanadium have been used separately and together in similar amounts (0.007-0.008 wt.%) in steels to refine grain size and achieve precipitation strengthening (microalloying)¹¹⁸. Additionally, grain size was not determined for experimental alloys in the oil quenched condition, which resulted in a more substantial increase in yield strength, though it is expected that grain size is not strongly dependent on quench rate from the austenitizing temperature.

Strengthening Precipitates – In order to understand the effect of nickel on strength, characterization of strengthening carbides was conducted using transmission electron microscopy (TEM). The heat treatment for specimens examined focused on an austenitizing temperature of 1050°C, air cooling, and a tempering temperature of 550°C, conditions which yielded monotonic effects of nickel during tensile testing. The initial hypothesis was that increasing nickel content would increase strength properties by refining the size and spacing of strengthening precipitates. However, due to the relatively insignificant increase in yield strength even at higher nickel levels, the effect of nickel content on strengthening carbides is not likely to be substantial. Based on published work on AerMet 100 and AF1410, the strengthening precipitates were expected to be fine Mo₂C needles 5-10 nm in length.

For both alloys examined, strengthening precipitates were fine needles, corresponding with streaking in the selected area diffraction patterns. In the 0% Ni alloy investigated, 011301, the strengthening precipitates were determined to be fine VC carbides, which followed the Nutting-Baker orientation relationships reported in other vanadium containing secondary hardening steels. Using dark field TEM images, average carbide length was calculated to be 6.2 nm, comparable to length of carbides at peak strength in AerMet 100 and AF1410 by Ayer and Machmeir⁷⁸ (7.5 nm), Novotny¹¹³ (4.1-9.1 nm), and Yoo et al.¹¹⁴ (4.5-9.5 nm). Supplementary elemental mapping confirmed that these small carbides were predominantly vanadium but revealed some titanium and molybdenum incorporation into these particles. Mo₂C carbides were not detected in this alloy.

In 011291, the strengthening precipitates were determined to be Mo₂C type carbides. These carbides were finer and more closely spaced than the VC carbides observed in 011301. This data supports the initial hypothesis that nickel increases the nucleation rate of strengthening precipitates in these alloys. Additionally, the size of the Mo₂C carbides in this experimental alloy is much smaller, less than 1 nm on average, than those seen in AerMet 100 or AF1410 at peak strength, possibly due to a shorter tempering time.

The tensile testing data from 011301 and 011291, together with the carbide characterization, implies that nickel additions shift tempering reactions to higher temperatures and at a tempering temperature of 550°C, 011301 is over-aged. Previous research¹¹⁹ show that vanadium additions to molybdenum steels delay the rate of coarsening by forming VC carbides which are more stable than Mo₂C in over-aged conditions,

which could account for the high yield strength of 011301, despite the high tempering temperature.

7.2 Study II: Ductile-to-Brittle Transition Temperature

7.2.1 Effect of Heat Treatment

Tempering Temperature – The effect of tempering temperature on the DBTT was determined for all five experimental alloys (**Figures 7.3-7.7**). Charpy impact testing showed no significant effect of tempering temperature on the DBTT. While a difference in Charpy impact energy can be observed in the 011301 heat between tempering at 575°C and at 525°C and 550°C, the DBTT itself does not appear to change. At higher nickel levels, tempering temperature seemed to affect upper shelf temperature at high test temperatures, with upper shelf toughness decreasing with increasing tempering temperature (Figures 7.6-7.7).



Figure 7.3: Effect of tempering temperature on DBTT of 011480 (0% Ni, no RE).



Figure 7.4: Effect of tempering temperature on DBTT of 011301 (0% Ni).



Figure 7.5: Effect of tempering temperature on DBTT of 011164 (3% Ni)



Figure 7.6: Effect of tempering temperature on DBTT of 011291 (5% Ni).



Figure 7.7: Effect of tempering temperature on DBTT of 011481 (6% Ni).

Temper Cycles – DBTT curves for 011291 and 011481 in the single and triple tempered 550°C condition were constructed (Figures 6.5-6.6). The number of the temper cycles exhibited no effect on the DBTT for either nickel level. Upper shelf toughness did slightly decrease from the single to triple temper condition and this effect was greater in the 6% Ni alloy than the 5% Ni alloy.

7.2.2 Effect of Nickel Content

Ductile-to-Brittle Transition Temperature – Testing of Charpy impact specimens revealed that nickel did affect the DBTT, with DBTT decreasing with increasing nickel content as originally hypothesized. The effect of nickel can be seen most clearly at a tempering temperature of 550°C (Figure 6.3).

Charpy impact energy for 011301 (0% Ni) is low for most test temperatures and begins to increase when tested at 100°C, suggesting that the DBTT for this alloy is above the highest test temperature used. Conversely, the Charpy impact energies for the 5% and 6% Ni alloys are relatively high at most test temperatures, only significantly dropping when tested at liquid nitrogen temperatures, suggesting that the DBTT is near or below -194°C. The DBTT of the 3% Ni seems to be in between the 5% and 6% Ni and 0% Ni alloys, near -25°C.

In order to correlate DBTT estimates from the Charpy impact energy curves with changes in microstructural features, fracture surfaces of experimental alloys were examined using an SEM. A comparison of the room temperature fracture surfaces for three of the rare earth treated experimental alloys can be seen in **Figure 7.8**. Fracture mode changes from brittle for the 0% Ni to ductile for the 3% and 5% Ni alloys.



Figure 7.8: Fracture surface of broken Charpy impact specimens tested at room temperature of alloys (a) 011301, (b) 011164, and (c) 011291 austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at 575°C.

In **Figure 7.9**, the fracture surfaces of 011301 tested at room temperature and 100°C can be seen. As could be expected from the Charpy test results, the fracture surface is indicative of quasi-cleavage at room temperature. At a test temperature of 100°C, impact energy increases slightly but the fracture surface begins to exhibit ductile characteristics, which indicates a DBTT near 100°C.



Figure 7.9: Fracture surface of broken Charpy impact specimens of alloy 011301 austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at 550°C for test temperatures of (a) -80°C, (b) room temperature (23°C), and (c) 100°C.

Fracture surfaces of 011164 tested at -80° C, -40° C, 0° C, and room temperature (23°C) can be seen in **Figure 7.10**. At -80° C, the failure mode appears to be predominantly quasi-cleavage, while at room temperature, the fracture mode is fully ductile with both large and small voids observed on the fracture surface. At test temperatures of -40° C and 0° C, the fracture surfaces are similar. Fracture mode seems to be

quasi-cleavage with areas indicative of microvoid formation. Based on fractography, the DBTT for 011164 lies somewhere between -40° C and 0°C, which agrees with the estimate of -25° C from Charpy impact testing.



Figure 7.10: Fracture surface of broken Charpy impact specimens of alloy 011164 austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at 550°C for test temperatures of -80°C, -40°C, 0°C, and room temperature (23°C).

When looking at the fracture surfaces of the 011291, fracture mode is ductile, regardless of test temperature (**Figure 7.11**). Even at -80°C there is little evidence of quasi-cleavage, consistent with a DBTT below -80°C. Charpy impact energy increased almost 7 J from a test temperature of 0°C to room temperature, which can be correlated to a slight increase in size of voids between the two temperatures.



Figure 7.11: Fracture surface of broken Charpy impact specimens of alloy 011291 austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at 550°C for test temperatures of -80°C, 0°C, and room temperature (23°C).

The fracture surface of the 011481 (**Figure 7.12**) tested at -80°C is almost identical to that of 011291, evidence that in this alloy, fracture mode is ductile even at a low test temperature.





Figure 7.12: Fracture surface of broken Charpy impact specimen of alloy 011481 austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at 575°C for test temperatures of -80°C.

Upper Shelf Toughness – At a tempering temperature of 525°C, upper shelf toughness increased with increasing nickel content. However, at higher tempering temperatures, increasing nickel content resulted in decreased upper shelf toughness.

Martensite Start Temperature – Martensite start temperature was determined for 011301, 011164, and 011291. Increasing nickel content decreased the M_s temperature. An increase of 5% Ni decreased the M_s

temperature by 120°C, an average of 24°C/wt. % Ni. This data agrees well with Yeo's previous work in which the decrease in martensite start temperature was 26.5°C/wt. % Ni⁶.

Prior Austenite Grain Size – Any effect grain size might have on the DBTT is obscured by the strong dependence of DBTT on nickel content. Certainly, the DBTT does not agree with the correlation suggested by Jin or Kim's research (Section 2.4.3). However, perhaps the slightly lower Charpy impact energy of the 6% Ni heat at various points in the DBTT curve compared to the 5% Ni heat could be the result of 011291's finer grain size.

Retained Austenite – Based on nickel's ability to depress the martensite start temperature, one would expect the retained austenite content to increase with increasing nickel content. As discussed in Section 2.4.3, retained austenite can act to increase the DBTT. Retained austenite was measured in the as-quenched and 575°C triple tempered condition for the 011301, 011164, and 011291. In the as-quenched, pre-liquid nitrogen refrigerated condition, increasing nickel content increases retained austenite content in the microstructure. However, in the final triple tempered condition, the volume of retained austenite has been significantly reduced and is essentially equal for all three alloys. Therefore, the effect of differing amounts of retained austenite in the triple tempered condition on the DBTT in these experimental alloys can be considered negligible.

7.2.3 Effect of Inclusion Type

After the unexpectedly low Charpy impact energy at room temperature was revealed during initial mechanical testing of 011301, a new base alloy that was not rare earth treated during the melt practice was made (heat identification 011480). While the bulk of discussion on the mechanical behavior of 011480 is reserved for Section 7.3, a brief comparison of DBTT Charpy results of the two base alloys is included here.

At low test temperatures, both base alloys exhibit brittle facture and low Charpy impact energy. However, as test temperatures are increased, the rare earth free alloy 011480 has higher Charpy impact energies than its rare earth counterpart. This trend is seen regardless of tempering temperature (**Figures 7.13-7.15**), although it is more pronounced for triple tempering at 525°C and 550°C. As average inclusion size, volume fraction, and spacing for the two nickel-free alloys are nearly identical, the results of Charpy impact testing suggest that large inclusions act to increase the DBTT in the absence of nickel additions.



Figure 7.13: Results of DBTT testing for experimental base alloys austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at 525°C.



Figure 7.14: Results of DBTT testing for experimental base alloys austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at 550°C.



Figure 7.15: Results of DBTT testing for experimental base alloys austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen, and triple tempered at 575°C.

7.3 Study III: Fracture Toughness

7.3.1 Effect of Heat Treatment

Quench Rate – As observed with tensile testing, slowing the quench rate resulted in unexpected toughness properties. Increasing the quench rate resulted in an increase in room temperature Charpy impact energy (Figure 7.16), except for a nickel level of 5 wt.%. This can also be seen when comparing the K_{IC} fracture toughness of 011164, where toughness was approximately 15% lower for air cooled samples than oil quenched ones in all tempering conditions (Figure 7.17). A possible explanation for this behavior is that the martensite start temperature of these alloys is sufficiently high that relatively fine particles precipitate during a slow cool and these precipitates contribute to increased strength and reduced toughness upon tempering. The decrease in martensite start temperature with increasing nickel content could reduce the volume fraction of these precipitates for higher nickel additions, which would account for the smaller differences between tensile and fracture properties in air cooled and oil quenched samples with increasing nickel content. Further investigation into differences in the microstructure as a result of quench rate, both in the as-quenched and tempered conditions, is necessary to determine the cause of this unusual behavior.



Figure 7.16: Effect of quench rate of Charpy impact energy of samples austenitized at 1050°C and triple tempered at 575°C and tested at room temperature.



Figure 7.17: Effect of quench rate on K_{IC} fracture toughness of 011164 specimens austenitized at 1050°C and tested at room temperature.

Tempering Temperature – The effect of tempering temperature on room temperature toughness properties can be seen in the K_{IC} fracture data, in which toughness increased with increasing tempering temperature. The largest increase in toughness occurred from 525°C to 550°C. The effect of increasing tempering temperature to 550°C also increased with increasing nickel content. An increase in toughness was observed on increasing the tempering temperature from 550°C to 575°C for all alloys except 011481, whose toughness remained approximately equal for this change in tempering temperature.

Temper Cycles – No appreciable difference is observed between single and triple tempered Charpy impact specimens for 011291 and 011481. However, there is an increase in K_{IC} fracture toughness. 011291 exhibits a 5% increase in fracture toughness, while the effect of temper cycles is stronger in 011481, where going from a single to a triple temper increased the fracture toughness by 11%. Thus, multiple temper cycles has a slightly greater impact on fracture toughness in the highest nickel content than yield strength (approximately 6%).

7.3.2 Effect of Nickel Content

Charpy Impact Energy – It was hypothesized that Charpy impact energy would decrease with increasing nickel content, when the fracture mode was ductile, based on the results from preliminary work for this project. However, the opposite was found to be true – Charpy impact energy increased with increasing nickel content. For Charpy testing, the nickelfree base alloys generally had low toughness. For 3%, 5%, and 6% Ni additions, Charpy impact energies were moderately high and generally increased with increasing nickel content, regardless of heat treatment.

The low toughness of the rare-earth treated base steel 011301, 15 J, was of some surprise, considering its composition is nearly identical to that of the base alloy used in Garrison's previous study in which a Charpy impact energy of approximately 45 J was achieved for the same heat treatment conditions. Fractography of 011301 conducted in the SEM revealed, unsurprisingly, a brittle fracture surface with very few areas of small microvoids. Inclusion particles found in the fracture surface of the 0% Ni alloy were analyzed using EDS. Rare earth sulfides and oxysulfides were observed, as expected. However, chemistries of some of the inclusion particles revealed traces of titanium, which were also seen when inclusions were more extensively analyzed in polished crosssections of test specimens.

Examination of the fracture surfaces from broken Charpy impact specimens broken at room temperature from 011164 and 011291 were indicative of ductile fracture. Inclusions analyzed using EDS confirmed these particles to be rare earth sulfides, oxides, or oxysulfides. Of particular interest in the fracture surfaces were the areas of fine microvoids that appear at interfaces, indicated by the red arrows in **Figure 7.18**. It was thought that the morphology of these microvoid regions could correlate to sheets of inter-lath retained austenite that decomposed during the tempering process, resulting in fine carbides that nucleated voids at the lath interfaces. If these regions were associated with the decomposition of the retained austenite, microvoids could nucleate at martensite packet boundaries or along prior austenite grain boundaries. These fine void features were noted in fracture surfaces for all experimental alloys containing nickel and their area fraction initially appeared to increase with increasing nickel content.

For 011291, these interfacial microvoid regions also appear to increase with increasing tempering temperature (Figure 7.18). The Charpy impact energy increased from a tempering temperature of 525°C to 550°C but decreased when the tempering temperature was increased from a tempering temperature of 550°C and 575°C. The decrease in toughness

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at 575°C could be due to coarsening of these carbides formed on interfaces once they had become equiaxed.



Figure 7.18: Scanning electron micrograph of fracture surface of experimental alloy 011291 austenitized at 1050°C, air cooled, refrigerated in liquid nitrogen and triple tempered at (a) 525, (b) 550°C, and (c) 575°C.

However, based on the results summarized in Table 6.8, area fraction of secondary voids did not change significantly with either nickel content or tempering temperature.

 K_{IC} Fracture Toughness – Fracture toughness was assessed for all five experimental alloys austenitized at 1050°C, air cooled, and triple tempered at 525°C, 550°C, and 575°C. As with the corresponding Charpy samples, the nickel-free alloys exhibited poor toughness. For the 011480 heat, the degree of brittleness caused several specimens to fracture prior to testing during pre-crack fabrication. Toughness increased dramatically with the addition of nickel. For these alloys, fracture toughness decreased when nickel content increased from 3% to 5% but increased when nickel content was increased from 5% to 6%. The 3% Ni heat had the highest toughness when samples were tempered at 525°C and 575°C. The 6% Ni heat had the highest toughness at a tempering temperature at 550°C. Therefore, peak tensile and toughness properties were reached at a nickel level of 6% and triple tempering at 550°C. *Fine-Scale Microstructure* – Based on initial inspection of broken Charpy impact specimens discussed above, it was thought that fine microvoid areas visible in the fracture surfaces were the result of carbide particles that precipitated during tempering due to the decomposition of retained austenite. This hypothesis was supported by the XRD measurements, which showed that increasing nickel content increased retained austenite content prior to tempering. In order to determine the effect of nickel content and heat treatment on the area fraction of these microvoid regions, fracture surfaces of K_{IC} specimens for all experimental alloys were analyzed using the point counting techniques outlined in Section 5.4. The results (Table 6.7) showed no correlation between nickel content or tempering temperature on microvoid area fraction. Therefore, these fine void regions cannot be definitively linked to the byproducts of retained austenite decomposition.

7.3.3 Effect of Inclusions

Nickel-Containing Alloys – For the three nickel-containing alloys, 011164, 011291, 011481, inclusion type was constant. However, inclusion characteristics (average radius, volume fraction, and particle spacing) did vary from alloy to alloy. The difference in fracture toughness in these alloys could be attributed in part to the effect of volume fraction per the Rice and Johnson model⁴⁷, which predicts an increase in δ_{IC} , i.e. increase in toughness, with increasing inclusion spacing or decreasing volume fraction, both of which were observed when nickel content was increased from 3% to 5%. As the particle spacing is relatively large for the rare-earth inclusion particles, the effect of spacing is likely small. The higher inclusion volume fraction of 011164 could account for as much as a 9% decrease in the K_{IC} fracture toughness, using the scaling proposed by Garrrison and Wojcieszynski¹²⁰ in which $K_{IC} \sim (1/f)^{1/6}$.

Nickel-Free Alloys – Two nickel-free base alloys, 011301 and 011480, were prepared for this study, each with a different inclusion population. The inclusions in these two heats are characterized in this section.

As previously mentioned, the rare-earth treated nickel-free alloy 011301 was contaminated during melting. This resulted in five inclusion categories:

Type 1 – "Pure" rare-earth inclusions

Type 2 – Rare-earth inclusions with titanium incorporation

Type 3 – "Pure" titanium inclusions

Type 4 – Titanium inclusions with rare earth incorporation

Type 5 - Other, e.g. calcium and aluminum oxides/sulfides

The percent of the total inclusions encountered in 011301 for each type can be seen in **Figure 7.19**. The characteristics for the five inclusion types are listed in **Table 7.1**. The majority of the inclusion particles were of the rare-earth dominant type. Inclusions containing rare-earths were slightly larger in size than titanium-containing inclusions. Type 5 particles were significantly larger on average than other inclusions but their volume fraction was low; thus their overall contribution to total inclusion characteristics was negligible.



Figure 7.19: Inclusion types found in 011301.

Inclusion Type	Average Radius (um)	Volume	
	Average Radius (µm)	Fraction	
Type 1	0.86	6.71E-05	
Type 2	0.76	6.65E-05	
Туре 3	0.69	4.12E-05	
Type 4	0.86	5.15E-06	
Type 5	1.86	2.11E-05	

Table 7.1: Average inclusion particle radius and volume fraction in 011301.

The second base alloy 011480 was produced in an attempt to replicate the original base steel from Garrison's previous work. The inclusions were expected to be fine chromium sulfides. However upon investigation, it was determined that the inclusions were predominantly large calcium and aluminum oxides (Figures 6.21-22, **Figure 7.20**, **Table 7.2**). Thus, the new base heat also suffered from contamination. As it happens, the previous heat to 011480 was calcium-treated and is likely the culprit of the calcium inclusions. The presence of aluminum appears to be the result of the crucibles used for melting, which were 88% Al₂O₃, as no aluminum was deliberately added as a de-oxidizing agent. Interestingly, no sulfide particles were observed in 011480. It is possible that fine sulfides are present in the material but could not be observed at the magnification used in this inclusion analysis.



Figure 7.20: Inclusion types found in 011480.

	Average	Volume	
inclusion Type	Radius (µm)	Fraction	
Calcium oxides	1.08	1.17E-04	
Aluminum oxides	0.56	3.28E-05	
Other	0.32	1.23E-05	

Table 7.2: Average inclusion particle radius and volume fraction in 011480.

Although the average inclusion size was roughly equivalent for both base alloys, the difference in toughness between these two alloys at room temperature cannot be directly attributed to any effect of inclusion volume fraction and particle spacing, as the Rice and Johnson model applies only to materials in which ductile fracture dominates. It is also possible that the rare-earth inclusions in 011301 are more detrimental to toughness than the inclusions in 011480 because rare-earth inclusions have very low coefficients of thermal expansion in general and lower coefficients of thermal expansion than the inclusions in 011480. Research by Brooksbank and Andrews⁶⁶ found that the coefficient of thermal expansion of inclusion particles dictated the direction and severity of residual stresses relative to the matrix. If the coefficient of thermal expansion of the inclusions was smaller than the matrix, circumferential stresses would be tensile. If the coefficient of thermal expansion of the inclusions was greater than the matrix, the circumferential stresses would be compressive. Tensile circumferential stresses should assist in the nucleation of quasi-cleavage fracture and promote low toughness (Figure 7.21).



Figure 7.21: Circumferential stress fields around inclusion particles due to thermal expansion coefficients. Adapted from D.Brooksbank and K.W. Andrews⁶⁶.

Comparison to Previous Nickel-Free Alloys – In earlier work, Garrison investigated two different series of 0.4 wt.% carbon secondary hardening steels. The first series was comprised of three steels of the composition 0.4C-XCr-2Mo-0.5V, where X = 3, 4, 5. The second series of three steels contained a lower molybdenum content, and the compositions were 0.4C-XCr-1.3Mo-0.5V, where X = 3, 4, 5. These nickel-free steels in all series had excellent Charpy impact energies (about 40 J) when tempered at 550°C.

The high toughness of these steels is perplexing given the low Charpy impact energies of the two nickel-free alloys considered here, heats 011301 and 011480. We believe that the heats 011301 and 011480 had a much lower toughness than the earlier heats prepared by Garrison because the inclusions in these experimental heats were large and brittle and are responsible for the quasi-cleavage fracture observed for these heats. The inclusions in three of the earlier heats prepared by Garrison were analyzed. Compositions of these heats can be seen in **Table 7.3**. The inclusions in these three heats have been characterized using SEM analysis of polished cross-sections. Due to the small inclusion size, a magnification of 5000X was used. Results obtained at this magnification are summarized in the table below (Table 7.3).

Heat ID	Composition	Average Radius (μm)	Volume Fraction	Average Particle Spacing (μm)
80-5-6	0.38C-5Cr-2Mo-0.5V	0.108	5.43E-04	1.18
80-5-7	0.39C-3Cr-1.3Mo-0.5V	0.097	3.91E-04	1.18
80-5-8	0.39C-4Cr-1.3Mo-0.5V	0.166	3.99E-04	2.00

Table 7.3: Inclusion analysis of nickel-free alloys from earlier work of Garrison.

Analysis indicates that the inclusions in the earlier heats of Garrison are very small relative to inclusions seen in this experimental work. Garrison's alloys also contain larger inclusions ($R_0 = 0.643 \mu$ m), characterized at a magnification of 1000X, but the small volume fractions of these particles (f = 3.98E-05) mean they have little contribution to the overall toughness. The particle spacing was also much lower than the experimental base heats used in this work, which correlates to conclusions made by Maloney⁷⁰ regarding the effect of rare earth elements on particle spacing. These results suggest that for these nickel-free alloys, inclusion size has the greatest effect on toughness, rather than volume fraction or particle spacing and that the low toughness of the 011301 and 011480 is due to their large inclusion size. It is believed that these large and brittle inclusions fracture and nucleate quasi-cleavage, resulting in very poor toughness.

8. CONCLUSIONS

8.1 Study I: Strength

The results of tensile testing supported the hypothesis that increasing nickel content will increase the strength. Characterization of strengthening precipitates indicates that the fine precipitates of VC and Mo₂C contribute to the strength of these steels.

Peak strength in the experimental alloys was reached by austenitizing at 1050°C, air cooling, and triple tempering at 550°C in the nickel containing alloys. The highest strength levels in nickel-free alloys were achieved when tempering at 525°C. Strengthening precipitates in 011301 were identified as VC carbides approximately 6.2 nm in length. Strengthening precipitates in 011291 were identified as Mo₂C carbides approximately 0.9 nm in length. The effect of vanadium additions to a molybdenum secondary hardening steel could explain the high strength of 011301, despite being heat treated to an over-aged condition. Decreasing the cooling rate by air cooling instead of oil quenching from the austenitizing temperature resulted in higher strength for experimental alloys and this effect was strongly dependent on nickel content.

8.2 Study II: Ductile-to-Brittle Transition Temperature

The DBTT for all experimental alloys were estimated using Charpy impact testing for specimens air cooled from the austenitizing temperature and triple tempered at 525°C, 550°C, and 575°C. Heat treatment condition did not have a significant effect on the DBTT. Increasing the nickel content from 0 wt.% to 5 and 6 wt.% decreased the DBTT by approximately 200°C, which supports the hypothesis for Study II. The contributions of prior austenite grain size and retained austenite content to the DBTT were negligible. The low toughness of the two heats containing no nickel and the high DBTT of these heats is attributed to the large inclusions in these alloys. It is felt that these particles fracture and nucleate quasi-cleavage fracture in the steel matrix. When comparing the two base steels, it appears that rare earth inclusions are slightly more effective in promoting quasi-cleavage than calcium and aluminum oxide inclusions of comparable size.

8.3 Study III: Fracture Toughness

The original hypothesis that toughness would decrease with increasing nickel content was proven false for these alloys. Charpy impact energy increased with increasing nickel content. The base alloys exhibited unexpectedly low Charpy impact energy compared to previous work in heats with nearly identical composition. Analysis of the new and old nickel-free alloys showed that the difference in toughness was due primarily to inclusion particle size. The difference in toughness of the two base alloys which contain no nickel could be due to the low coefficient of thermal expansion for the rare-earth inclusions, which could increase tensile circumferential stresses at the inclusions hat promote quasi-cleavage. Examination of K_{IC} fracture surfaces revealed no correlation between average area fraction of secondary voids and fracture toughness.

9. RECOMMENDATIONS FOR FUTURE WORK

Optimizing and Understanding Mechanical Properties – The yield strength and K_{IC} fracture toughness at peak strength in the air cooled condition were less than necessary for the experimental heats to be adequate alternatives to current commercial alloys like AerMet 100. More work is needed to determine if these mechanical properties can be increased to a comparable level. This could be explored two ways: adjusting heat treatment and composition.

Given tempering times and sizes of strengthening carbides at peak strength in AerMet 100 and AF1410, the results of this work suggest that a single temper with a longer tempering time could be used to optimize precipitation of strengthening carbides in the experimental alloys and increase yield strength. Additionally, oil quenching fracture properties were only determined for 011164. The results of that work indicate that fracture toughness higher than that of AerMet 100 could be achieved at a nickel level of only 5 wt.%. Although oil quenching was shown to reduce yield strength and ultimate tensile strength of these experimental alloys, the effect of quench rate decreased with increasing nickel content and at higher nickel levels, 5 and 6 wt.%, it may be possible to achieve sufficient yield strength at longer tempering times while maintaining excellent toughness. Secondly, composition could be modified to increase strength, specifically through increased chromium content, which Garrison has shown can increase strength without sacrificing toughness.

As only one tempering curve was constructed for 011164, completing tempering curves would be useful for confirming peak tempering temperature for 011291 and 011481 and determining peak tempering temperature, hardness, and strength for the base alloys.

It is unclear why no Mo₂C carbides were observed in 011301, considering molybdenum is the primary secondary hardening alloying addition. A more complete investigation into the strengthening precipitates as a result of heat treatment in these alloys is recommended.

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During preliminary testing of 011164, stress corrosion testing was conducted to compare the experimental alloys to AerMet 100. The results of that study concluded that 011164 had superior corrosion resistance. It would be interesting to see if 011291 and 011481 had similarly excellent resistance to stress corrosion cracking.

Effect of Quench Rate on Mechanical Properties – An intriguing result of mechanical testing was that the increase in strength was dependent on the cooling rate from the austenitizing temperature. A slow cooling rate produced the highest strength levels and masked the effect of nickel additions observed in a faster oil quenched condition. It is hypothesized that the martensite start temperatures of these alloys could play a role in this phenomena. Further investigation into the microstructural mechanism behind the effect of cooling rate is necessary to fully explain this behavior. This would include characterization of precipitates in the experimental alloys in the as-quenched condition.

Effect of Inclusion Type on DBTT – DBTT curves of the two nickel-free base steels suggested that rare-earth additions contribute to an increase in the DBTT, possibly due to the low coefficients of thermal expansion for rare-earth inclusions compared to the calcium oxides observed in heat 011480. This hypothesis could be further tested by creating a new base steel engineered to contain inclusion particles with high coefficients of thermal expansion, according to the work by Brooksbank and Andrews.

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11. APPENDIX

AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	C _v (J)
1050	OIL	525	1525	1919	32.7	13.8
		550	1486	1857	65.6	15.0
	QUENCH	575	1527	1850	58.9	
		600	1459	1739	44.8	

Table A1: Averaged mechanical properties for oil-quenched, triple tempered 011301 specimens.

Table A2: Averaged mechanical properties for air cooled, triple tempered 011301 specimens.

AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	C _v (J)	K _{ɪc} (MPa√m)
		525	1624	2025	41.9	15.1	
1025		550	1587	1953	42.7	12.4	
	575	1555	1879	57.0	10.0		
	_						
		525	1637	2056	38.2	7.6	28.8
1050	AIR COOL	550	1573	1953	47.2	8.3	29.4
	_	575	1510	1846	51.5	8.7	31.6
	_						
1075	-	525	1551	2003	3.6	7.6	
		550	1498	1888	35.1	6.6	
		575	1505	1838	39.4	5.9	
Table A3: Averaged mechanical properties for oil-quenched, triple tempered 011164 specimens.

AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	С _v (J)	K _{ɪc} (MPa√m)
		200	1558	2078	8.0	22.9	
		300	1437	1916	22.9	34.1	
		400	1487	1927	29.1	17.5	
		450	1500	1951	32.6	19.0	
		475	1494	1980	30.6	20.3	
1050		500	1503	1996	42.9	22.5	
	QUENCI	525	1510	1972	55.0	25.2	109.5
		550	1555	1927	47.5	33.2	125.8
		560	1548	1917	42.0	34.0	
		575	1582	1879	65.0	34.2	145.1
		600	1409	1652	36.5	27.9	

Table A4: Averaged mechanical properties for air cooled, triple tempered 011164 specimens.

AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	C _v (J)	K _{IC} (MPa√m)
		525	1523	1948	52.5	24.5	
1025		550	1572	1924	56.5	29.1	
	_	575	1558	1843	55.0	26.4	
	_						
		525	1580	1991	44.0	24.0	97.1
1050	AIR COOL	550	1606	1976	54.0	23.1	108.3
	_	575	1566	1871	47.5	38.5	119.3
	_						
	-	525	1586	2003	40.0	20.8	
1075		550	1551	1951	50.0	23.1	
		575	1564	1870	38.5	35.0	

AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	C _v (J)	K _{ɪc} (MPa√m)
		525	1458	1979	46.0	25.3	
1050	AIR COOL	550	1448	1920	62.0	34.5	
		575	1517	1903	66.5	29.6	

Table A5: Averaged mechanical properties for air cooled, single tempered 011164 specimens.

Table A6: Averaged mechanical properties for oil-quenched, triple tempered 011291 specimens.

AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	C _v (J)
		525		2045	59.5	31.35
4050	OIL	550	1622	1974	59.9	40.9
1020	QUENCH	575	1439	1790	57.8	35.4
		600	1422	1559	43.2	27.45

Table A7: Averaged mechanical properties for air cooled, triple tempered 011291 specimens.

AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	C _v (J)	K _{ɪc} (MPa√m)
		525	1577	2009	56.0	39.1	
1025		550	1615	1991	54.5	56.0	
		575	1500	1787	48.5	43.5	
	_						
	_	525	1628	2082	48.0	29.5	86.1
1050	AIR COOL	550	1636	2014	56.5	50.5	104.9
	_	575	1532	1820	43.0	28.1	111.1
	_						
	-	525	1675	2122	45.0	23.0	
1075		550	1624	2014	40.0	38.4	
		575	1593	1877	27.5	19.3	

Table A8: Averaged mechanical properties for air cooled, triple tempered 011480 specimens.

AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	C _v (J)	K _{ɪc} (MPa√m)
1050	AIR COOL	525	1631	2077	26.2	8.4	28.1
		550	1593	1987	36.0	8.6	
		575	1575	1914	39.8	9.9	33.0

AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	C _v (J)	K _{ɪc} (MPa√m)
		525	1643	2072	42.7	25.1	91.6
1050	AIR COOL	550	1631	1977	44.9	23.8	113.8
		575	1533	2045	29.2	21.1	113.0

Table A9: Averaged mechanical properties for air cooled, triple tempered 011481 specimens.

Table A10: Averaged mechanical properties for air cooled, single tempered 011291 and 011481 specimens.

ALLOY ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	C _v (J)	K _{ɪc} (MPa√m)
011291	1050		550	1525	2027	32.3	28.9	99.3
011481	1030		330	1533	2045	25.0	23.5	101.8

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	EL (%)	TRUE FRACTURE STRAIN (mm/mm)
T30109	1050	OIL QUENCH	525	1507	1893	12	4.3	0.12
T30123	1050	OIL QUENCH	525	1542	1946	54	13.8	0.77
T30111	1050	OIL QUENCH	550	1486	1857	66	15.5	1.07
T30114	1050	OIL QUENCH	575	1527	1850	59	13.1	0.89
T30126	1050	OIL QUENCH	600	1459	1739	45	11.9	0.59

Table A11: Tensile properties for oil-quenched, triple tempered 011301 specimens austenitized at 1050°C.

Table A12: Tensile properties for air-cooled, triple tempered 011301 specimens austenitized at 1025°C.

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	EL (%)	TRUE FRACTURE STRAIN (mm/mm)
T30127	1025	AIR COOL	525	1596	2003	40	13.2	0.51
T30128	1025	AIR COOL	525	1651	2046	44	13.1	0.57
T30129	1025	AIR COOL	550	1577	1928	30	8.7	0.35
T30130	1025	AIR COOL	550	1598	1978	56	14.8	0.81
T30131	1025	AIR COOL	575	1555	1869	64	11.2	1.01
30132	1025	AIR COOL	575	1555	1889	50	12.8	0.70

Table A13: Tensile properties for air-cooled, triple tempered 011301 specimens austenitized at 1050°C.

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	EL (%)	TRUE FRACTURE STRAIN (mm/mm)
30135	1050	AIR COOL	525	1633	2084	40	10.9	0.51
30136	1050	AIR COOL	525	1641	2027	36	11.5	0.45
30137	1050	AIR COOL	550	1563	1942	49	13.2	0.68
30138	1050	AIR COOL	550	1584	1964	45	12.7	0.60
30140	1050	AIR COOL	575	1511	1832	49	13.0	0.67
30141	1050	AIR COOL	575	1509	1859	54	12.5	0.78

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	EL (%)	TRUE FRACTURE STRAIN (mm/mm)
30142	1075	AIR COOL	525	1595	2057	3	3.4	0.03
30143	1075	AIR COOL	525	1506	1949	4	5.5	0.04
30144	1075	AIR COOL	550	1499	1905	32	10.6	0.38
30145	1075	AIR COOL	550	1497	1871	39	13.0	0.49
30146	1075	AIR COOL	575	1482	1840	39	11.9	0.49
30147	1075	AIR COOL	575	1528	1836	40	11.4	0.51

Table A14: Tensile properties for air-cooled, triple tempered 011301 specimens austenitized at 1075°C.

Table A15: Tensile properties for oil-quenched, triple tempered 011164 specimens austenitized at 1025°C or 1075°C.

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	EL (%)	TRUE FRACTURE STRAIN (mm/mm)
6427	1000	OIL QUENCH	550	1544	1875	56	15	0.8
6421	1000	OIL QUENCH	550	1503	1896	59	15.2	0.9
6428	1000	OIL QUENCH	575	1510	1827	64	15.6	1.0
6429	1000	OIL QUENCH	575	1510	1793	46	9.5	0.6
6420	1075	OIL QUENCH	550	1579	1937	65	15.9	1.0
6422	1075	OIL QUENCH	550	1579	1937	62	15.5	1.0

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	TEMP. CYCLE	YS (MPa)	UTS (MPa)	RA (%)	EL (%)	TRUE FRACTURE STRAIN (mm/mm)
6401	1050	OIL QUENCH	200	TRIPLE	1546	2044	10	1.7	0.1
6402	1050	OIL QUENCH	200	TRIPLE	1570	2111	6	3.8	0.1
6403	1050	OIL QUENCH	300	TRIPLE	1439	1914	26	7.6	0.3
6404	1050	OIL QUENCH	300	TRIPLE	1436	1918	20	7.1	0.2
6405	1050	OIL QUENCH	400	TRIPLE	1769	1925	30	<u>9.1</u>	0. 4
6406	1050	OIL QUENCH	400	TRIPLE	1487	1928	28	9.5	0.3
6413**	1050	OIL QUENCH	450	TRIPLE	1504	1948	30	10.4	0.4
6414**	1050	OIL QUENCH	450	TRIPLE	1495	1954	36	12.1	0.4
6407	1050	OIL QUENCH	475	TRIPLE	1493	1977	29	11.5	0.3
6408	1050	OIL QUENCH	475	TRIPLE	1495	1983	32	11.5	0.4
64N	1050	OIL QUENCH	500	TRIPLE	1511	1996	42	11.9	0.5
64X	1050	OIL QUENCH	500	TRIPLE	1496	1996	44	13.5	0.6
6444	1050	OIL QUENCH	525	SINGLE	1455	1965	49	14.8	0.7
6446	1050	OIL QUENCH	525	SINGLE	1462	1993	43	14.0	0.6
646	1050	OIL QUENCH	525	TRIPLE	1531	1972	55	15.4	0.8
647	1050	OIL QUENCH	525	TRIPLE	1489	1972	55	15.5	0.8
6440	1050	OIL QUENCH	550	SINGLE	1434	1931	62	16.0	1.0
6442	1050	OIL QUENCH	550	SINGLE	1462	1910	61	15.7	0.9
648	1050	OIL QUENCH	550	TRIPLE	1551	1910	31	12.7	0.4
649	1050	OIL QUENCH	550	TRIPLE	1558	1944	64	15.8	1.0

Table A16: Tensile properties for oil-quenched 011164 specimens austenitized at 1050°C.

1050	OIL QUENCH	560	TRIPLE	1579	1937	47	13.4	0.6
1050	OIL QUENCH	560	TRIPLE	1517	1896	37	11.3	0.5
1050	OIL QUENCH	575	SINGLE	1503	1903	67	16.1	1.1
1050	OIL QUENCH	575	SINGLE	1531	1903	66	16.1	1.1
1050	OIL QUENCH	575	TRIPLE	1579	1882	65	15.6	1.0
1050	OIL QUENCH	575	TRIPLE	1586	1875	65	15.7	1.0
1050	OIL QUENCH	600	TRIPLE	1416	1660	34	9.6	0.4
1050	OIL QUENCH	600	TRIPLE	1402	1644	39	10.1	0.5
1050	OIL QUENCH	T550+500	TRIPLE+10HR	1613	1951	65	15.6	1.0
1050	OIL QUENCH	T550+500	TRIPLE+10HR	1600	1965	65	15.7	1.0
1050	OIL QUENCH	T575+500	TRIPLE+10HR	1579	1868	67	15.7	1.1
1050	OIL QUENCH	T575+500	TRIPLE+10HR	1586	1882	65	15.5	1.0
	1050 1050 1050 1050 1050 1050 1050 1050	1050 OIL QUENCH 1050 OIL QUENCH	1050 OIL QUENCH 560 1050 OIL QUENCH 575 1050 OIL QUENCH 600 1050 OIL QUENCH 600 1050 OIL QUENCH 7550+500 1050 OIL QUENCH 7550+500 1050 OIL QUENCH 757+500 1050 OIL QUENCH 757+500	1050OIL QUENCH560TRIPLE1050OIL QUENCH560TRIPLE1050OIL QUENCH575SINGLE1050OIL QUENCH575SINGLE1050OIL QUENCH575TRIPLE1050OIL QUENCH575TRIPLE1050OIL QUENCH600TRIPLE1050OIL QUENCH600TRIPLE1050OIL QUENCH7550+500TRIPLE+10HR1050OIL QUENCH1550+500TRIPLE+10HR1050OIL QUENCH1575+500TRIPLE+10HR1050OIL QUENCH1575+500TRIPLE+10HR1050OIL QUENCH1575+500TRIPLE+10HR	1050 OIL QUENCH 560 TRIPLE 1579 1050 OIL QUENCH 560 TRIPLE 1517 1050 OIL QUENCH 575 SINGLE 1503 1050 OIL QUENCH 575 SINGLE 1531 1050 OIL QUENCH 575 SINGLE 1579 1050 OIL QUENCH 575 TRIPLE 1579 1050 OIL QUENCH 575 TRIPLE 1586 1050 OIL QUENCH 600 TRIPLE 1416 1050 OIL QUENCH 600 TRIPLE 1402 1050 OIL QUENCH 750+500 TRIPLE+10HR 1613 1050 OIL QUENCH 755+500 TRIPLE+10HR 1600 1050 OIL QUENCH 757+500 TRIPLE+10HR 1579 1050 OIL QUENCH 757+500 TRIPLE+10HR 1579	1050 OIL QUENCH 560 TRIPLE 1579 1937 1050 OIL QUENCH 560 TRIPLE 1517 1896 1050 OIL QUENCH 575 SINGLE 1503 1903 1050 OIL QUENCH 575 SINGLE 1531 1903 1050 OIL QUENCH 575 SINGLE 1531 1903 1050 OIL QUENCH 575 TRIPLE 1579 1882 1050 OIL QUENCH 575 TRIPLE 1586 1875 1050 OIL QUENCH 600 TRIPLE 1416 1660 1050 OIL QUENCH 600 TRIPLE 1402 1644 1050 OIL QUENCH 7550+500 TRIPLE+10HR 1613 1951 1050 OIL QUENCH 7550+500 TRIPLE+10HR 1600 1965 1050 OIL QUENCH 7575+500 TRIPLE+10HR 1579 1868 1050 OIL QUENCH 7575+500 TRIPLE+10HR 1586 1882	1050OIL QUENCH560TRIPLE15791937471050OIL QUENCH560TRIPLE15171896371050OIL QUENCH575SINGLE15031903661050OIL QUENCH575SINGLE15311903661050OIL QUENCH575TRIPLE15791882651050OIL QUENCH575TRIPLE15861875651050OIL QUENCH600TRIPLE14161660341050OIL QUENCH600TRIPLE14021644391050OIL QUENCH7550+500TRIPLE+10HR16131951651050OIL QUENCH755+500TRIPLE+10HR15791868671050OIL QUENCH7575+500TRIPLE+10HR1586188265	1050OIL QUENCH560TRIPLE157919374713.41050OIL QUENCH560TRIPLE151718963711.31050OIL QUENCH575SINGLE150319036616.11050OIL QUENCH575SINGLE153119036616.11050OIL QUENCH575TRIPLE157918826515.61050OIL QUENCH575TRIPLE158618756515.71050OIL QUENCH600TRIPLE14161660349.61050OIL QUENCH600TRIPLE140216443910.11050OIL QUENCH7550+500TRIPLE+10HR161319516515.71050OIL QUENCH1550+500TRIPLE+10HR160019656515.71050OIL QUENCH1575+500TRIPLE+10HR157918686715.71050OIL QUENCH1575+500TRIPLE+10HR158618826515.5

Table A17: Tensile properties for air-cooled 011164 specimens austenitized at 1025°C.

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	EL (%)	TRUE FRACTURE STRAIN (mm/mm)
6417	1025	AIR COOL	525	1530	1950	50	13.7	0.69
6418	1025	AIR COOL	525	1516	1945	55	15.8	0.80
6470	1025	AIR COOL	550	1544	1915	59	14.8	0.89
6471	1025	AIR COOL	550	1600	1932	54	13.9	0.78
6472	1025	AIR COOL	575	1555	1842	53	13.7	0.76
6473	1025	AIR COOL	575	1562	1843	57	14.4	0.84

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	EL (%)	TRUE FRACTURE STRAIN (mm/mm)
6476	1050	AIR COOL	525	1574	1992	45	13.2	0.60
6477	1050	AIR COOL	525	1585	1989	43	11.5	0.56
6478	1050	AIR COOL	550	1580	1971	56	14.7	0.82
6479	1050	AIR COOL	550	1632	1980	52	12.7	0.73
6481	1050	AIR COOL	575	1545	1844	43	11.8	0.56
6482	1050	AIR COOL	575	1587	1897	52	13.9	0.73

Table A18: Tensile properties for air-cooled, triple tempered 011164 specimens austenitized at 1050°C.

Table A19: Tensile properties for air-cooled, triple tempered 011164 specimens austenitized at 1075°C.

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	EL (%)	TRUE FRACTURE STRAIN (mm/mm)
6483	1075	AIR COOL	525	1804	1985	38	11.6	0.48
6484	1075	AIR COOL	525	1586	2020	42	11.2	0.54
6485	1075	AIR COOL	550	1517	1947	49	11.6	0.67
6486	1075	AIR COOL	550	1584	1955	51	12.8	0.71
6487	1075	AIR COOL	575	1577	1876	37	9.5	0.46
6488	1075	AIR COOL	575	1552	1863	40	10.2	0.51

Table A20: Tensile properties for oil-quenched, triple tempered 011291 specimens austenitized at 1050°C.

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	EL (%)	TRUE FRACTURE STRAIN (mm/mm)
29110	1050	OIL QUENCH	525	1826	2045	60	14.1	0.90
29111	1050	OIL QUENCH	550	1622	1974	60	13.2	0.91
29113	1050	OIL QUENCH	575	1528	1799	54	12.4	0.79
29126	1050	OIL QUENCH	575	1349	1781	61	14.4	0.94
29127	1050	OIL QUENCH	600	1518	1546	43	11.4	0.56
29115	1050	OIL QUENCH	600	1326	1572	43	10.7	0.57

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	TRUE FRACTURE STRAIN (mm/mm)
291A1	1050	AC	550	1537	2033	33	0.40
291A2	1050	AC	550	1533	2043	29	0.34
291A3	1050	AC	550	1515	2006	34	0.41
291A4	1050	AC	550	1513	2026	34	0.41

Table A21: Tensile properties for oil-quenched, single tempered 011291 specimens austenitized at 1050°C.

Table A22: Tensile properties for air-cooled, triple tempered 011291 specimens.

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	EL (%)	TRUE FRACTURE STRAIN (mm/mm)
29128	1025	AIR COOL	525	1589	2010	56	14.8	0.82
29129	1025	AIR COOL	525	1564	2007	56	15.0	0.82
29130	1025	AIR COOL	550	1619	1981	54	13.5	0.78
29131	1025	AIR COOL	550	1611	2000	55	14.0	0.80
29134	1025	AIR COOL	575	1506	1784	48	12.2	0.65
29135	1025	AIR COOL	575	1493	1790	49	12.9	0.67
29136	1050	AIR COOL	525			dam	aged samp	le
29137	1050	AIR COOL	525	1628	2082	48	12.8	0.65
<u>29138</u>	1050	AIR COOL	550	1795	2008	56	12.9	0.82
29139	1050	AIR COOL	550	1636	2020	57	14.5	0.84
29140	1050	AIR COOL	575	1532	1823	45	12.0	0.60
29141	1050	AIR COOL	575	1531	1816	41	10.9	0.53
29144	1075	AIR COOL	525	1690	2133	46	12.2	0.62
29145	1075	AIR COOL	525	1660	2110	44	12.1	0.58
29146	1075	AIR COOL	550	1577	1981	38	10.0	0.48
29147	1075	AIR COOL	550	1670	2046	42	11.3	0.54
29148	1075	AIR COOL	575	1562	1838	27	6.4	0.31
29149	1075	AIR COOL	575	1625	1915	28	7.7	0.33

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	TRUE FRACTURE STRAIN (mm/mm)
011480-3	1050	AIR COOL	525	1605	2053	23	0.26
011480-4	1050	AIR COOL	525	1630	2055	27	0.31
480 17	1050	AIR COOL	525	1633	2098	27	0.31
480 18	1050	AIR COOL	525	1654	2101	28	0.33
480 9	1050	AIR COOL	525	1569	2045	28	0.32
480 12	1050	AIR COOL	525	1619	2047	22	0.24
480 8	1050	AIR COOL	525	1600	2041	24	0.27
480 14	1050	AIR COOL	525	1589	2039	25	0.28
011480-2	1050	AIR COOL	550	1600	1996	36	0.44
011480-15	1050	AIR COOL	550	1612	2006	34	0.42
480 1	1050	AIR COOL	550	1576	1970	33	0.40
480 5	1050	AIR COOL	550	1598	1991	37	0.46
480 13	1050	AIR COOL	550	1580	1957	41	0.52
011480-11	1050	AIR COOL	575	1574	1890	37	0.45
011480-7	1050	AIR COOL	575	1565	1919	39	0.49
480 16	1050	AIR COOL	575	1586	1932	44	0.59

Table A23: Tensile properties for air-cooled, triple tempered 011480 specimens austenitized at 1050°C.

Table A24: Tensile properties for air-cooled, single tempered 011481 specimens austenitized at 1050°C.

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	TRUE FRACTURE STRAIN (mm/mm)
481A1	1050	AIR COOL	550	1510	2040	28	0.33
481A2	1050	AIR COOL	550	1559	2044	28	0.32
481A3	1050	AIR COOL	550	1549	2057	20	0.22
481A4	1050	AIR COOL	550	1515	2038	25	0.28

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	YS (MPa)	UTS (MPa)	RA (%)	TRUE FRACTURE STRAIN (mm/mm)
011481-15	1050	AIR COOL	525	1625	2058	49	0.67
011481-7	1050	AIR COOL	525	1632	2068	47	0.64
481 18	1050	AIR COOL	525	1627	2062	43	0.57
481 16	1050	AIR COOL	525	1640	2069	38	0.48
481 14	1050	AIR COOL	525	1665	2072	41	0.52
481 4	1050	AIR COOL	525	1649	2079	43	0.57
481 2	1050	AIR COOL	525	1662	2096	37	0.46
011481-8	1050	AIR COOL	550	1614	1966	48	0.64
011481-13	1050	AIR COOL	550	1646	1976	49	0.68
011481-11	1050	AIR COOL	550	1640	1988	44	0.57
011481-3	1050	AIR COOL	550	1629	1978	42	0.55
481 12	1050	AIR COOL	550	1626	1979	42	0.54
011481-1	1050	AIR COOL	575	1509	1793	34	0.41
011481-5	1050	AIR COOL	575	1515	1764	27	0.31
481 6	1050	AIR COOL	575	1521	1765	27	0.32

Table A25: Tensile properties for air-cooled, triple tempered 011481 specimens austenitized at 1050°C.

ID	TEMPERING TEMP	K _{ıc} (ksi√in)	K _{IC} (MPa√m)	VALID
K30102	525	27.4	30.1	YES
K30105	525	25	27.5	YES
K30101	550	26.6	29.2	YES
K30106	550	27	29.7	YES
K30104	575	28.2	31.0	YES
K30103	575	29.3	32.2	YES

Table B1: K_{IC} properties for air-cooled, triple tempered 011301 specimens austenitized at 1050°C.

Table B2: K_{IC} properties for oil-quenched 011164 specimens.

ID	AUST. (°C)	QUENCH	TEMP. (°C)	TEMP. CYCLE	K _{ıc} (MPa√m)	VALID
K644	1000	OIL QUENCH	550	TRIPLE	122.2	YES
K643	1000	OIL QUENCH	550	TRIPLE	115.9	NO
K6412	1050	OIL QUENCH	525	TRIPLE	110.4	YES
K6411	1050	OIL QUENCH	525	TRIPLE	108.6	YES
K6410	1050	OIL QUENCH	550	TRIPLE	128.5	YES
К649	1050	OIL QUENCH	550	TRIPLE	123.1	YES
K648	1050	OIL QUENCH	575	TRIPLE	144.7	YES
K647	1050	OIL QUENCH	575	TRIPLE	145.4	YES
K645	1050	OIL QUENCH	T575+500	TRIPLE+10HR	144.1	YES
KC46	1050	OIL QUENCH	T575+500	TRIPLE+10HR	143.6	NO

ID	TEMPERING TEMP	K _{ıc} (ksi√in)	K _{ıc} (MPa√m)	VALID
K6450	525	88.9	97.7	YES
K6470	525	87.9	96.6	YES
K6471	550	98.9	108.7	YES
K6460	550	98.3	108.0	YES
K6461	575	109.9	120.8	YES
K6451	575	107.3	117.9	YES

Table B3: K_{IC} properties for air-cooled, triple tempered 011164 specimens austenitized at 1050°C.

Table B4: K_{IC} properties for air-cooled, triple tempered 011291 specimens austenitized at 1050°C.

ID	TEMPERING TEMP	K _{ıc} (ksi√in)	K _{ıc} (MPa√m)	VALID
K29105	525	81.2	89.2	YES
K29102	525	75.6	83.1	YES
K29101	550	89.2	98.0	YES
K29108	550	101.7	111.8	NO
K29106	575	100.9	110.9	YES
K29107	575	101.3	111.3	YES

ID	TEMPERING TEMP	K _{ıc} (ksi√in)	K _{ıc} (MPa√m)	VALID
K4802	525	25.1	27.6	NO
K4806	525	26.1	28.7	YES
K4803	575	30.4	33.4	YES
K4804	575	29.7	32.6	YES

Table B5: K_{IC} properties for air-cooled, triple tempered 011480 specimens austenitized at 1050°C.*

*All K_{ic} samples for 011480 triple tempered at 550°C failed during pre-crack initiation.

Table B6: K_{IC} properties for air-cooled, triple tempered	ed 011481 specimens austenitized at 1050°C.
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ID	TEMPERING TEMP	K _{ıc} (ksi√in)	K _{ıc} (MPa√m)	VALID
K4819	525	81.4	89.4	YES
K4813	525	85.3	93.7	YES
K4811	550	103.7	113.9	YES
K4812	550	103.5	113.7	YES
K4818	575	102.9	113.1	YES
K4814	575	102.7	112.9	YES

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	C _v (J)	COMMENTS
C30109	1050	OIL QUENCH	525	12.1	FORGING FLAW
C31010	1050	OIL QUENCH	525	15.5	
C31011	1050	OIL QUENCH	550	11.9	FORGING FLAW
C31013	1050	OIL QUENCH	550	18	
C30124	1025	AIR COOL	525	13.5	
C30125	1025	AIR COOL	525	16.7	
C30126	1025	AIR COOL	550	11.8	
C30127	1025	AIR COOL	550	13.0	
C30128	1025	AIR COOL	575	10.0	
C30129	1025	AIR COOL	575	9.9	
C30132	1050	AIR COOL	525	7.0	
C30133	1050	AIR COOL	525	8.1	
C30134	1050	AIR COOL	550	8.5	
C30135	1050	AIR COOL	550	8.0	
C30137	1050	AIR COOL	575	8.1	
C30138	1050	AIR COOL	575	9.2	
C30140	1075	AIR COOL	525	7.4	
C30141	1075	AIR COOL	525	7.7	
C30142	1075	AIR COOL	550	6.7	
C30143	1075	AIR COOL	550	6.5	
C30144	1075	AIR COOL	575	14.0	
C30145	1075	AIR COOL	575	5.9	

Table C1: Charpy impact properties for triple tempered 011301 specimens.

ID	AUST. (°C)	QUENCH	TEMP. (°C)	TEMP. CYCLE	C _v (J)	COMMENTS
C641	1000	OIL QUENCH	525	TRIPLE	36.5	
C642	1000	OIL QUENCH	525	TRIPLE	35	
C643	1000	OIL QUENCH	550	TRIPLE	38	
C644	1000	OIL QUENCH	550	TRIPLE	37.9	b, 0.03
C649	1000	OIL QUENCH	575	TRIPLE	41.7	
C6410	1000	OIL QUENCH	575	TRIPLE	54.4	f to s, 0.02
C6401	1050	OIL QUENCH	200	TRIPLE	26	
C6403	1050	OIL QUENCH	200	TRIPLE	19.7	
C6406	1050	OIL QUENCH	300	TRIPLE	15.9	
C64X	1050	OIL QUENCH	300	TRIPLE	18.2	FORGING FLAW
C6411**	1050	OIL QUENCH	400	TRIPLE	17.5	
C6418	1050	OIL QUENCH	400	TRIPLE	5.9	
C6413**	1050	OIL QUENCH	450	TRIPLE	19.4	
C6415**	1050	OIL QUENCH	450	TRIPLE	18.6	
C6417**	1050	OIL QUENCH	475	TRIPLE	18.9	
C6420**	1050	OIL QUENCH	475	TRIPLE	20.9	FORGING FLAW
C6424	1050	OIL QUENCH	475	TRIPLE	19.9	
C6425	1050	OIL QUENCH	475	TRIPLE	21.6	
C6440	1050	OIL QUENCH	500	SINGLE	22	f, 0.02
C6443	1050	OIL QUENCH	500	SINGLE	19.3	
C6426	1050	OIL QUENCH	500	TRIPLE	22.1	
C6421	1050	OIL QUENCH	500	TRIPLE	22.8	
C6446	1050	OIL QUENCH	525	SINGLE	27.4	
C6447	1050	OIL QUENCH	525	SINGLE	23.2	
C6422	1050	OIL QUENCH	525	TRIPLE	24.3	

Table C2: Charpy impact properties for oil-quenched 011164 specimens.

C6423	1050	OIL QUENCH	525	TRIPLE	26.1	b, 0.12
C6442	1050	OIL QUENCH	550	SINGLE	38.5	
C6449	1050	OIL QUENCH	550	SINGLE	33.8	
C6445	1050	OIL QUENCH	550	SINGLE	31.1	
C6411*	1050	OIL QUENCH	550	TRIPLE	35.3	
C6412	1050	OIL QUENCH	550	TRIPLE	31.1	b, 0.10
C6413*	1050	OIL QUENCH	560	TRIPLE	29.9	b, 0.10
C6417*	1050	OIL QUENCH	560	TRIPLE	38.1	f to s, 0.15
C6444	1050	OIL QUENCH	575	SINGLE	29.3	
C6448	1050	OIL QUENCH	575	SINGLE	29.9	
C6419	1050	OIL QUENCH	575	TRIPLE	35.6	b, 0.03
C6420*	1050	OIL QUENCH	575	TRIPLE	32.7	b, 0.02
C6409	1050	OIL QUENCH	600	TRIPLE	29	
C6410	1050	OIL QUENCH	600	TRIPLE	26.7	
C6414	1050	OIL QUENCH	T550+500	TRIPLE+10HR	30.5	b, 0.10
C6415*	1050	OIL QUENCH	T550+500	TRIPLE+10HR	28.4	
C6416	1050	OIL QUENCH	T575+500	TRIPLE+10HR	36.8	b, 0.10
C6427	1050	OIL QUENCH	T575+500	TRIPLE+10HR	34.2	f, 0.02
C6428	1075	OIL QUENCH	525	TRIPLE	26.9	
C6429	1075	OIL QUENCH	525	TRIPLE	24.6	b, 0.10
C6430	1075	OIL QUENCH	550	TRIPLE	32	f, 0.15
C646	1075	OIL QUENCH	550	TRIPLE	32.8	f, 0.10
C647	1075	OIL QUENCH	575	TRIPLE	29.7	
C648	1075	OIL QUENCH	575	TRIPLE	38	s, 0.10

ID	AUST. (°C)	QUENCH	TEMPER (°C)	C _v (J)
C6417	1025	AIR COOL	525	27.9
C6418	1025	AIR COOL	525	21.0
C6470	1025	AIR COOL	550	29.1
C6471	1025	AIR COOL	550	29.0
C6472	1025	AIR COOL	575	26.1
C6473	1025	AIR COOL	575	26.7
C6476	1050	AIR COOL	525	22.1
C6477	1050	AIR COOL	525	25.8
C6478	1050	AIR COOL	550	24.0
C6479	1050	AIR COOL	550	22.1
C6481	1050	AIR COOL	575	39.0
C6483	1050	AIR COOL	575	38.0
C6484	1075	AIR COOL	525	19.2
C6485	1075	AIR COOL	525	22.3
C6486	1075	AIR COOL	550	23.9
C6487	1075	AIR COOL	550	22.2
C6488	1075	AIR COOL	575	42.0
C6489	1075	AIR COOL	575	35.0

Table C3: Charpy impact properties for triple tempered air-cooled 011164 specimens.

ID	AUST. (°C)	QUENCH	TEMPER (°C)	C _v (J)	COMMENTS
C29109	1050	OIL QUENCH	525	36.0	
C29110	1050	OIL QUENCH	525	26.7	
C29111	1050	OIL QUENCH	550	39.5	FORGING FLAW
C29112	1050	OIL QUENCH	550	42.3	
C29114	1050	OIL QUENCH	575	41.0	FORGING FLAW
C29125	1050	OIL QUENCH	575	29.8	
C29126	1050	OIL QUENCH	600	24.8	
C29115	1050	OIL QUENCH	600	30.1	FORGING FLAW
C29127	1025	AIR COOL	525	42.1	
C29128	1025	AIR COOL	525	36.0	
C29129	1025	AIR COOL	550	52.0	
C29130	1025	AIR COOL	550	60.0	
C29133	1025	AIR COOL	575	47.9	
C29134	1025	AIR COOL	575	39.0	
C29135	1050	AIR COOL	525	29.0	
C29136	1050	AIR COOL	525	30.0	
C29137	1050	AIR COOL	550	48.0	
C29138	1050	AIR COOL	550	53.0	
C29139	1050	AIR COOL	575	27.9	
C29140	1050	AIR COOL	575	28.2	
C29143	1075	AIR COOL	525	22.0	
C29144	1075	AIR COOL	525	23.9	
C29145	1075	AIR COOL	550	45.5	
C29146	1075	AIR COOL	550	31.3	
C29147	1075	AIR COOL	575	18.0	
C29148	1075	AIR COOL	575	20.5	

Table C4: Charpy impact properties for triple tempered 011291 specimens.

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	TEST TEMP. (°C)	C _v (J)
C301 D24	1050	AIR COOL	525	-194	1.4
C301 47	1050	AIR COOL	525	-120	2.7
C301 46	1050	AIR COOL	525	-80	2.7
C301 D27	1050	AIR COOL	525	-80	2.7
C301 31	1050	AIR COOL	525	-40	2.7
C301 26	1050	AIR COOL	525	-40	4.1
C301 D28	1050	AIR COOL	525	0	2.7
C301 D22	1050	AIR COOL	525	0	2.7
C301 30	1050	AIR COOL	525	21	4.1
C301 D23	1050	AIR COOL	525	21	4.1
C301 39	1050	AIR COOL	525	100	6.8
C301 25	1050	AIR COOL	525	100	5.4

Table D1: Charpy impact properties for air-cooled DBTT specimens for 011301 austenitized at 1050°C and triple tempered at 525°C.

Table D2: Charpy impact properties for air-cooled DBTT specimens for 011301 austenitized at 1050°C and triple tempered at 550°C.

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	TEST TEMP. (°C)	C _v (J)
C301 D14	1050	AIR COOL	550	-194	2.7
C301 D16	1050	AIR COOL	550	-120	2.7
C301 D20	1050	AIR COOL	550	-80	1.4
C301 D12	1050	AIR COOL	550	-80	2.7
C301 D21	1050	AIR COOL	550	-40	2.7
C301 D18	1050	AIR COOL	550	-40	2.7
C301 D11	1050	AIR COOL	550	0	2.7
C301 D10	1050	AIR COOL	550	0	4.1
C301 D17	1050	AIR COOL	550	21	4.7
C301 D15	1050	AIR COOL	550	21	5.4
C301 D13	1050	AIR COOL	550	100	5.4
C301 D19	1050	AIR COOL	550	100	6.8

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	TEST TEMP. (°C)	C _v (J)
C301 D33	1050	AIR COOL	575	-194	2.7
C301D1	1050	AIR COOL	575	-80	3.4
C301D2	1050	AIR COOL	575	-80	5.4
C301D3	1050	AIR COOL	575	-40	4.6
C301D4	1050	AIR COOL	575	-40	5.7
C301D5	1050	AIR COOL	575	0	6.1
C301D6	1050	AIR COOL	575	0	5.6
C30137	1050	AIR COOL	575	23	8.1
C30138	1050	AIR COOL	575	23	9.2
C301D7	1050	AIR COOL	575	100	8.1
C301D8	1050	AIR COOL	575	100	11.5

Table D3: Charpy impact properties for air-cooled DBTT specimens for 011301 austenitized at 1050°C and triple tempered at 575°C.

Table D4: Charpy impact properties for air-cooled DBTT specimens for 011164 austenitized at 1050°C and triple tempered at 525°C.

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	TEST TEMP. (°C)	C _v (J)
C64D35	1050	AIR COOL	525	-194	6.8
C6401	1050	AIR COOL	525	-120	8.1
C6475	1050	AIR COOL	525	-120	9.5
C6474	1050	AIR COOL	525	-80	12.2
C6403	1050	AIR COOL	525	-80	10.8
C64 16	1050	AIR COOL	525	-40	16.3
C64 02	1050	AIR COOL	525	-40	16.3
C64 15	1050	AIR COOL	525	0	21.7
C64D34	1050	AIR COOL	525	0	20.3
C64 04	1050	AIR COOL	525	0	16.3
C64 05X	1050	AIR COOL	525	21	20.3
1050	AIR COOL	525	21	23.1	
 1050	AIR COOL	525	100	29.8	
 1050	AIR COOL	525	100	29.8	

C64 C64 C64

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	TEST TEMP. (°C)	C _v (J)
C64D38	1050	AIR COOL	550	-194	4.1
C64D14	1050	AIR COOL	550	-120	8.1
C64D19	1050	AIR COOL	550	-120	8.1
C64D15	1050	AIR COOL	550	-80	12.2
C64D11	1050	AIR COOL	550	-80	12.2
C64 D16	1050	AIR COOL	550	-40	16.3
C64 D21	1050	AIR COOL	550	-40	16.3
C64 D17	1050	AIR COOL	550	0	21.7
C64 D13	1050	AIR COOL	550	0	21.7
C64 D18	1050	AIR COOL	550	21	26.4
C64D39	1050	AIR COOL	550	21	23
C64 D12	1050	AIR COOL	550	21	19
C64 D10	1050	AIR COOL	550	100	29.8
C64D37	1050	AIR COOL	550	100	24.4
C64D20	1050	AIR COOL	550	100	36.6

Table D5: Charpy impact properties for air-cooled DBTT specimens for 011164 austenitized at 1050°C and triple tempered at 550°C.

	IC	D AUST. (°C)	QUENCH METHOD	TEMPER (°C	C) TEST TE (°C
C64D24	1050	AIR COOL	575	-194	5.4
C64D27	1050	AIR COOL	575	-120	8.1
C64D22	1050	AIR COOL	575	-120	8.1
C64D1	1050	AIR COOL	575	-80	11.5
C64D2	1050	AIR COOL	575	-80	8.8
C64D3	1050	AIR COOL	575	-40	16.3
C64D4	1050	AIR COOL	575	-40	16.7
C64 D25	1050	AIR COOL	575	-40	16.3
C64 D26	1050	AIR COOL	575	0	19.0
C64D5	1050	AIR COOL	575	0	19.3
C64D6	1050	AIR COOL	575	0	19.0
C6481	1050	AIR COOL	575	21	39.0
C6483	1050	AIR COOL	575	21	38.0
C64 D28	1050	AIR COOL	575	21	19
C64D43	1050	AIR COOL	575	21	33.9

Table D6: Charpy impact properties for air-cooled DBTT specimens for 011164 austenitized at 1050°C and triple tempered at 575°C.

		D AUST. (°C)	QUENCH METHOD	TEMPER (°C)	TEST TE (°C)
C291 D43	1050	AIR COOL	525	-194	8.1
C291 31	1050	AIR COOL	525	-120	10.8
C291 D28	1050	AIR COOL	525	-120	12.2
C291 D31	1050	AIR COOL	525	-80	14.9
C291 D42	1050	AIR COOL	525	-80	16.3
C291 D26	1050	AIR COOL	525	-80	24.4
C291 D23	1050	AIR COOL	525	-40	19
C291 D22	1050	AIR COOL	525	-40	20.3
C291 32	1050	AIR COOL	525	0	27.1
C291 D41	1050	AIR COOL	525	0	27.1
C291 D29	1050	AIR COOL	525	0	17.6
C291 D25	1050	AIR COOL	525	21	27.1
C291 D24	1050	AIR COOL	525	21	29.2
C291 27	1050	AIR COOL	525	100	31.2
C291 30	1050	AIR COOL	525	100	31.2

Table D7: Charpy impact properties for air-cooled DBTT specimens for 011291 austenitized at 1050°C and triple tempered at 525°C.

	11	D AUST. (°C)	QUENCH METHOD	TEMPER (°C)	TEST TEMP. (°C)	С _v (J)
C291 D46	1050	AIR COOL	550	-194	8.1	
C291 D16	1050	AIR COOL	550	-120	16.3	
C291 D17	1050	AIR COOL	550	-120	17.6	
C291 D15	1050	AIR COOL	550	-80	20.3	
C291 D48	1050	AIR COOL	550	-80	19	
C291 D20	1050	AIR COOL	550	-80	35.3	
C291 D13	1050	AIR COOL	550	-40	4 6.1	
C291 D47	1050	AIR COOL	550	-40	19	
C291 D19	1050	AIR COOL	550	-40	24.4	
C291 D10	1050	AIR COOL	550	0	27.1	
C291 D21	1050	AIR COOL	550	0	29.8	
C291 D11	1050	AIR COOL	550	21	25.8	
C29145	1050	AIR COOL	550	21	28.5	
C291 D18	1050	AIR COOL	550	21	26.4	
C291 D12	1050	AIR COOL	550	100	29.8	
C291 D14	1050	AIR COOL	550	100	29.8	

Table D8: Charpy impact properties for air-cooled DBTT specimens for 011291 austenitized at 1050°C and triple tempered at 550°C.

		D AUST. (°C)	QUENCH METHOD	TEMPER (°	C) TEST TI (°C	EMP.	С _v (J)
C291 D36	1050	AIR COOL	575	-194	8.1		
C291 D33	1050	AIR COOL	575	-120	13.6		
C291 D40	1050	AIR COOL	575	-120	9.5		
C291 D34	1050	AIR COOL	575	-80	16.3		
C291D1	1050	AIR COOL	575	-80	19.0		
C291D2	1050	AIR COOL	575	-80	16.3		
C291D3	1050	AIR COOL	575	-40	19.3		
C291D4	1050	AIR COOL	575	-40	17.0		
C291 D52	1050	AIR COOL	575	-40	17.6		
C291 D32	1050	AIR COOL	575	-40	23.1		
C291 D51	1050	AIR COOL	575	0	28.5		
C291 D35	1050	AIR COOL	575	0	24.4		
C291D5	1050	AIR COOL	575	0	21.0		
C291D6	1050	AIR COOL	575	0	21.7		
C291 D37	1050	AIR COOL	575	21	20.3		
C29149	1050	AIR COOL	575	21	20.3		
C29150	1050	AIR COOL	575	21	20.3		
C291 D38	1050	AIR COOL	575	21	21.7		
C29139	1050	AIR COOL	575	21	27.9		
C29140	1050	AIR COOL	575	21	28.2		
C291 D39	1050	AIR COOL	575	100	25.8		
C291D7	1050	AIR COOL	575	100	25.8		
C291D8	1050	AIR COOL	575	100	23.9		

Table D9: Charpy impact properties for air-cooled DBTT specimens for 011291 austenitized at 1050°C and triple tempered at 575°C.

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	TEST TEMP. (°C)	C^ (J)
480 C6	1050	AIR COOL	525	-194	2.7
480 C11	1050	AIR COOL	525	-120	2.7
480 C23	1050	AIR COOL	525	-120	2.7
480 C53	1050	AIR COOL	525	-80	4.1
480 C30	1050	AIR COOL	525	-80	4.1
480 C22	1050	AIR COOL	525	-40	5.4
480 C44	1050	AIR COOL	525	-40	5.4
480 C5	1050	AIR COOL	525	-40	6.8
480 C1	1050	AIR COOL	525	0	5.4
480 C4	1050	AIR COOL	525	0	5.4
480 C64	1050	AIR COOL	525	0	8.1
480 C47	1050	AIR COOL	525	21	8.8
480 C3	1050	AIR COOL	525	21	6.8
480 C8	1050	AIR COOL	525	21	9.5
480 C50	1050	AIR COOL	525	100	10.8
480 C21	1050	AIR COOL	525	100	10.8

Table D10: Charpy impact properties for air-cooled DBTT specimens for 011480 austenitized at 1050°C and triple tempered at 525°C.

			ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	TEST TEMP. (°C)	C _v (J)
480 C46	1050	AIR COOL	550	-194	1.4			
480 C48	1050	AIR COOL	550	-120	2.7	<u> </u>		
480 C49	1050	AIR COOL	550	-120	2.7	-		
480 C56	1050	AIR COOL	550	-80	4.1	-		
480 C35	1050	AIR COOL	550	-80	4.1	<u> </u>		
480 C51	1050	AIR COOL	550	-40	4.1	<u> </u>		
480 C40	1050	AIR COOL	550	-40	5.4	-		
480 C65	1050	AIR COOL	550	-40	6.8	<u> </u>		
480 C41	1050	AIR COOL	550	0	5.4	-		
480 C26	1050	AIR COOL	550	0	8.1	-		
480 C2	1050	AIR COOL	550	0	8.1	<u> </u>		
480 C39	1050	AIR COOL	550	21	9.5	<u> </u>		
480 C29	1050	AIR COOL	550	21	9.5	-		
480 C25	1050	AIR COOL	550	21	6.8	-		
480 C28	1050	AIR COOL	550	100	13.6	-		
480 C24	1050	AIR COOL	550	100	14.9	-		

Table D11: Charpy impact properties for air-cooled DBTT specimens for 011480 austenitized at 1050°C and triple tempered at 550°C.

			ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	TEST TEMP. (°C)	C _v (J)
480 C19	1050	AIR COOL	575	-194	2.7			
480 C54	1050	AIR COOL	575	-120	5.4	•		
480 C55	1050	AIR COOL	575	-120	4.1	•		
480 C59	1050	AIR COOL	575	-80	4.1	•		
480 C10	1050	AIR COOL	575	-80	4.1	•		
480 C58	1050	AIR COOL	575	-40	5.4	•		
480 C36	1050	AIR COOL	575	-40	4.1	•		
480 C61	1050	AIR COOL	575	-40	6.8	<u>.</u>		
480 C32	1050	AIR COOL	575	0	8.1	•		
480 C20	1050	AIR COOL	575	0	10.8	•		
480 C38	1050	AIR COOL	575	0	9.5	<u>.</u>		
480 C52	1050	AIR COOL	575	21	10.8	<u>.</u>		
480 C9	1050	AIR COOL	575	21	9.5	-		
480 C33	1050	AIR COOL	575	21	9.5	-		
480 C34	1050	AIR COOL	575	100	14.9	-		
480 C31	1050	AIR COOL	575	100	12.2	-		

Table D12: Charpy impact properties for air-cooled DBTT specimens for 011480 austenitized at 1050°C and triple tempered at 575°C.

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	TEST TEMP. (°C)	C _v (J)	COMMENTS
481 C43	1050	AIR COOL	525	-194	4.1	
481 C16	1050	AIR COOL	525	-120	9.5	no argon
481 C58	1050	AIR COOL	525	-120	14.9	
481 C46	1050	AIR COOL	525	-120	9.5	
481 C15	1050	AIR COOL	525	-80	13.6	no argon
481 C80	1050	AIR COOL	525	-80	17.6	
481 C36	1050	AIR COOL	525	-80	12.2	
481 C12	1050	AIR COOL	525	-40	20.3	no argon
481 C85	1050	AIR COOL	525	-40	17.6	
481 C8	1050	AIR COOL	525	-40	17.6	
481 C42	1050	AIR COOL	525	0	24.4	no argon
481 C41	1050	AIR COOL	525	0	24.4	
481 C56	1050	AIR COOL	525	0	17.6	
481 C37	1050	AIR COOL	525	0	17.6	
481 C2	1050	AIR COOL	525	21	24.4	no argon
481 C74	1050	AIR COOL	525	21	24.4	
481 C3	1050	AIR COOL	525	21	25.8	
481 C25	1050	AIR COOL	525	100	21.7	no argon
481 C88	1050	AIR COOL	525	100	36.6	
481 C5	1050	AIR COOL	525	100	23	
481 C83	1050	AIR COOL	525	100	46.1	

Table D13: Charpy impact properties for air-cooled DBTT specimens for 011481 austenitized at 1050°C and triple tempered at 525°C.

	ID	AUST. (°C)	QUENCH	METHOD	TEMPER (°C)	TEST TEM	P. (°C)	С _v (J)	COMMENTS
481 C79	1050	AIR	COOL	550	-19	94	8.1		
481 C22	1050	AIR	COOL	550	-12	20	8.1	no arg	on
481 C82	1050	AIR	COOL	550	-12	20	13.6		
481 C59	1050	AIR	COOL	550	-12	20	12.2		
481 C84	1050	AIR	COOL	550	-12	20	16.3		
481 C62	1050	AIR	COOL	550	-8	0	12.2	no arg	on
481 C34	1050	AIR	COOL	550	-8	0	12.2	no arg	on
481 C51	1050	AIR	COOL	550	-8	0	14.9		
481 C19	1050	AIR	COOL	550	-8	0	16.3		
481 C64	1050	AIR	COOL	550	-4	0	14.9	no arg	on
481 C55	1050	AIR	COOL	550	-4	0	20.3	no arg	on
481 C54	1050	AIR	COOL	550	-4	0	14.9		
481 C47	1050	AIR	COOL	550	-4	0	17.6		
481 C67	1050	AIR	COOL	550	C		17.6	no arg	on
481 C14	1050	AIR	COOL	550	C		21.7	no arg	on
481 C39	1050	AIR	COOL	550	C)	21.7		
481 C50	1050	AIR	COOL	550	C		21.7		
481 C48	1050	AIR	COOL	550	2	1	20.3	no arg	on
481 C90	1050	AIR	COOL	550	2	1	23.1		
481 C30	1050	AIR	COOL	550	2	1	24.4		
481 C21	1050	AIR	COOL	550	10	0	23.1		
481 C17	1050	AIR	COOL	550	10	0	25.8		

Table D14: Charpy impact properties for air-cooled DBTT specimens for 011481 austenitized at 1050°C and triple tempered at 550°C.

	ID	AUST. (°C)	QUENCH I	METHOD	TEMPER (°C)	TEST TE	EMP. (°C)	C _v (J)	COMMENTS
481 C61	1050	AIR	COOL	575	-19	94	6.8		
481 C1	1050	AIR	COOL	575	-12	20	10.8	no arg	zon
481 C20	1050	AIR	COOL	575	-12	20	13.6		
481 C81	1050	AIR	COOL	575	-12	20	14.9		
481 C11	1050	AIR	COOL	575	-8	0	12.2	no arg	gon
481 C86	1050	AIR	COOL	575	8	0	20.3		
481 C28	1050	AIR	COOL	575	-8	0	10.8		
481 C18	1050	AIR	COOL	575	-8	0	13.6		
481 C52	1050	AIR	COOL	575	-4	0	13.6	no arg	gon
481 C69	1050	AIR	COOL	575	-4	0	14.9	no arg	gon
4 81 C87	1050	AIR	COOL	575	-4	θ	31.2		
481 C13	1050	AIR	COOL	575	-4	0	16.3		
481 C31	1050	AIR	COOL	575	-4	0	13.6		
481 C49	1050	AIR	COOL	575	()	17.6	no arg	zon
481 C79	1050	AIR	COOL	575	()	17.6		
481 C23	1050	AIR	COOL	575	()	16.3		
481 C35	1050	AIR	COOL	575	2	1	17.6	no arg	gon
481 C10	1050	AIR	COOL	575	2	1	23.1		
481 C27	1050	AIR	COOL	575	2	1	19		
481 C45	1050	AIR	COOL	575	10	00	20.3		
481 C26	1050	AIR	COOL	575	10	00	24.4		

Table D15: Charpy impact properties for air-cooled DBTT specimens for 011481 austenitized at 1050°C and triple tempered at 575°C.

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	TEST TEMP. (°C)	C _v (J)
291 AC1	1050	AIR COOL	550	-194	9.5
291 AC2	1050	AIR COOL	550	-120	13.6
291 AC3	1050	AIR COOL	550	-120	14.9
291 AC4	1050	AIR COOL	550	-120	10.8
291AC5	1050	AIR COOL	550	-80	17.6
291AC6	1050	AIR COOL	550	-80	19.0
291ACC7	1050	AIR COOL	550	-80	19.0
291AC8	1050	AIR COOL	550	-40	21.7
291AC9	1050	AIR COOL	550	-40	23.0
291AC10	1050	AIR COOL	550	-40	21.7
291AC11	1050	AIR COOL	550	θ	56.9
291AC12	1050	AIR COOL	550	0	21.7
291AC13	1050	AIR COOL	550	0	25.8
291AC14	1050	AIR COOL	550	21	27.1
291AC15	1050	AIR COOL	550	21	32.5
291AC16	1050	AIR COOL	550	21	27.1
291AC17	1050	AIR COOL	550	100	31.2
291AC18	1050	AIR COOL	550	100	33.9
291AC19	1050	AIR COOL	550	100	31.2

Table D16: Charpy impact properties for air-cooled DBTT specimens for 011291 austenitized at 1050°C and single tempered at 550°C.

ID	AUST. (°C)	QUENCH METHOD	TEMPER (°C)	TEST TEMP. (°C)	С _v (J)	COMMENTS
481 C61	1050	AIR COOL	575	-194	6.8	
481 C1	1050	AIR COOL	575	-120	10.8	no argon
481 C20	1050	AIR COOL	575	-120	13.6	
481 C81	1050	AIR COOL	575	-120	14.9	
481 C11	1050	AIR COOL	575	-80	12.2	no argon
481 C86	1050	AIR COOL	575	80	20.3	
481 C28	1050	AIR COOL	575	-80	10.8	
481 C18	1050	AIR COOL	575	-80	13.6	
481 C52	1050	AIR COOL	575	-40	13.6	no argon
481 C69	1050	AIR COOL	575	-40	14.9	no argon
481 C87	1050	AIR COOL	575	-40	31.2	
481 C13	1050	AIR COOL	575	-40	16.3	
481 C31	1050	AIR COOL	575	-40	13.6	
481 C49	1050	AIR COOL	575	0	17.6	no argon
481 C79	1050	AIR COOL	575	0	17.6	
481 C23	1050	AIR COOL	575	0	16.3	
481 C35	1050	AIR COOL	575	21	17.6	no argon
481 C10	1050	AIR COOL	575	21	23.1	
481 C27	1050	AIR COOL	575	21	19	
481 C45	1050	AIR COOL	575	100	20.3	
481 C26	1050	AIR COOL	575	100	24.4	

Table D17: Charpy impact properties for air-cooled DBTT specimens for 011481 austenitized at 1050°C and single tempered at 550°C.