THE FORMATION OF FERRITE IN IRON-NICKEL METEORITES

A Thesis in
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by
Raymond Matthew DeFrain, Jr.

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The thesis of Raymond Matthew DeFrain, Jr. was reviewed and approved* by the following:

Paul R. Howell  
Professor of Metals Science  
Thesis Advisor

Zi-Kui Liu  
Professor of Materials Science and Engineering

Christopher Muhlstein  
Assistant Professor of Materials Science and Engineering

Gary L. Messing  
Department Head and Professor of Materials Science and Engineering

*Signatures are on file in the Graduate School
ABSTRACT

The iron-nickel meteorites we find on Earth represent cores of planets, which have formed billions of years ago, but more importantly allow the researcher to view a metallographic sample which has cooled like no other terrestrial steel. The cooling rate of meteorites, from their initial liquid metal state to an ambient temperature has occurred on the order of 1 °C per million years. This heat treatment creates an alloy which nears the thermodynamic equilibrium, which our theories predict. Therefore, meteorites are ideal specimens for the researcher and metallurgist to study alike, considering their alien, near-optimal, inherent phase transformations.

In this thesis, the Cape York, Henbury, and Brenham meteorites are studied in an attempt to characterize the structures found within each sample. Moreover, many forms of ferrite are described within this report and may act as argument points as to multimodal ferrite nucleation. Finally, nucleation and growth methods of Widmanstätten ferrite are discussed as crystallography and morphology are used as guidelines to base our assumptions. Characterization methods used in this study include light microscopy, scanning electron microscopy, energy dispersive spectroscopy, electron probe micro-analysis, and orientational imaging microscopy.
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CHAPTER 1: METEORITES

1.1. INTRODUCTION

The meteorites we find on Earth represent cores or mantles of planets, which have formed billions of years ago. Meteorite fragments allow the researcher to view a metallographic sample which has cooled like no other terrestrial steel. The cooling rate of meteorites, from their initial liquid metallic state to an ambient temperature has occurred on the order of 1 °C per million years. This heat treatment creates an alloy which nears thermodynamic equilibrium. Therefore, meteorites are ideal specimens for metallurgists to study, considering their alien, near-equilibrium phase transformations.

In this thesis, the Canyon Diablo, Cape York, Henbury, and Brenham meteorites are characterized in terms of the structures found within each sample. Moreover, many forms of ferrite are described throughout this thesis and an argument for multimodal ferrite nucleation is presented. Finally, nucleation and growth modes of Widmanstätten ferrite are discussed; crystallography and morphology are used as guidelines to base our assumptions. Characterization methods used in this study include light microscopy, scanning electron microscopy, energy dispersive spectroscopy, electron probe micro-analysis, wavelength dispersive spectroscopy, and orientational imaging microscopy. Further details of experimental methods, including sample preparation, etchants used, and characterization techniques are given in Appendix A.
1.2. METEORITIC HISTORY, FORMATION, AND COMPOSITION

Our solar system consists of many bodies in elliptical orbits around the Sun. Each of these bodies and the star they orbit were formed from dust, ice, and clouds of particles nearly four and a half billion years ago [1]. Although our solar system contains, for the most part, bodies of spherical shape — located at specific distances away from the sun, there is a region of the solar system that contains a dense number of asymmetrical shaped bodies, namely asteroids, possibly where a planet once was.

Asteroids are large, irregularly-shaped, mineral masses and for the most part, are found between Jupiter and Mars in a region aptly named the asteroid belt [1]. This belt contains on the order of 1,000,000 asteroids, ranging in size from one km to nearly 950 km in diameter [2]. Although many of the asteroids orbit the sun unscathed for millennia, oftentimes the large gravity field from Jupiter, or a collision with another asteroid, ejects an asteroid from its normal path [2]. These ejecta, with modified trajectories, could now be on a collision course with another planet or celestial body. In the case of meteorites, these asteroids are on a path towards Earth, forming meteors (also known as shooting stars) on their entry (see figure 1.1).
Meteors are heated to an extremely high temperature on entry, due to the friction created by our planet’s gaseous atmosphere quickly decelerating the object, which either sears the outside “skin” of the rock or completely disintegrates it [1]. The objects that survive contact with our atmosphere and collide with our planet’s surface are called meteorites [1]. According to NASA, 10,000 tons of meteoritic material fall on Earth each day, although most of this is in the form of micron-sized dustings leftover from burn-up during entry [2].

Meteorites offer something to the scientific world that no other object on Earth can: timeless, near steady state existence. Meteorites not only give scientists the ability to look at specimens that exhibit near equilibrium in regards to phase transformations and crystal habits of specific species, but also the ability to peer into the past at a system that was created at the dawn of time and allowed to cool at incredibly slow rates.
As stated earlier, our solar system began to form roughly 4.5 billion years ago. At this time, tiny dust particles formed throughout the solar system, which eventually accreted into what are called chondrules – found in most every chondritic meteorite [4]. Chondrules are the microscopic and molten droplets of material, which originally were found nearly everywhere in our solar system [4]. Subsequently, gases and chondrules formed large discs of matter, which eventually began to gravity-spin and heat to a large enough degree to collapse in upon itself, creating a proto-star. This proto-star would later become our Sun (see figure 1.2) [4]. In other regions of the disc, the remaining dense areas of chondrules continued to accrete until large bodies, namely planetismals, began to take shape (see figure 1.2) [4]. As planets (or planetismals) formed, the clues to the young universe were locked into the buildup of the new “parent” body, “because tiny quantities of unprocessed pre-solar material have been found in the matrices of some chondritic meteorites that have never become strongly heated.” [5]

Meteorites are often associated with a “parent” body, i.e. the body in which the meteorite originated. Each meteorite has been categorized into groups based on their “fingerprint” of inherent elements, compounds, and structures. This allows meteoritic finds from different geological locations to be associated with the same parent body. Information regarding rare-earth elemental levels such as germanium (Ge) and gallium (Ga) has also grouped almost all meteoritic finds into three to four unique clusters [6]. Therefore, it is not difficult to imagine
that these different clusters of meteorites may have come from different parent bodies [6].

Figure 1.2 illustrates the origins of meteorites. Figure 1.2 a) shows a solar nebula, which consists of a ring of dust and gas particles (b), later this debris accumulates to form planetismals (c). The continued assembly produces a primitive planetesimal (d), which represents a relatively low amount of accumulation of chondritic material (small, spherical crystallized minerals formed in the nebula). This amount of material is not large enough to regionally differentiate heavier elements to the center; however (e) represents a much larger amount of accretion, where the increased amount of heavier elements yields the...
ability for differentiation. Heating, created by the high abundance of radioactive metals and the overall size of the planet body, caused the heavier elements to melt (e) [5]. As this heating occurred, the planetismal differentiated, pushing the heavier elements toward the center, which formed a metallic core (f). This core, which has had the ability to cool at an incredibly slow rate, is oftentimes what meteoritic metallurgists study. Meteoritic metallurgists study three types of meteorites, namely stoney, stoney-iron, and iron meteorites. These three variants come from specific locations within a meteorite (g): the mantle, core-mantle boundary or core.

1.3 AN INTRODUCTION TO WIDMANSTÄTTEN FERRITE IN METEORITES

When studying meteorites, scientists collect a fragment of a planetismal, and by cutting the surface away, reveal what has been untouched for billions of years. Although only chondritic meteorites can give clues into the near beginnings of the solar system, iron meteorites offer a plethora of information for metallurgists through the analysis of the metallic phases. Development of specific iron phases, such as ferrite1, austenite2, and martensite3 are of qualities and sizes unrivaled by terrestrial steels. An understanding of the maturity of these microstructures (and many more) in iron-nickel meteorites could lead to an

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1 The body-centered cubic form of iron denoted in literature by the Greek letter alpha (α).
2 The face-centered cubic form of iron denoted in literature by the Greek letter alpha (γ).
3 A distorted body-centered tetragonal form of iron denoted in literature by the Greek letter alpha (α2). This species forms by shear and is responsible for the hardness in rapidly quenched steels.
understanding of the history and environment of the pre-solar universe. Some of these structures, at least for an iron meteorite, are shown figure 1.3.

Figure 1.3: An iron-nickel meteorite that has been cut, polished, and etched to reveal the large Widmanstätten structure, evident to the naked eye because of the very slow cooling rate of a meteorite [1].

In this illustration, the iron-nickel meteorite has been cut, polished, and etched allowing the large crystals of Widmanstätten ferrite to be seen with the naked eye, something only possible in meteorites. Although science obviously has many reasons for studying meteorites, this thesis will focus on the metallurgical attributes of iron-nickel meteorites and the near thermodynamic time scale associated with their microconstituents.

Iron meteorites have had a very long and interesting history – forming 4.5 billion years ago as cores of planetismals, the iron meteorites we study eventually found their way on a collision course with Earth. However, to
properly describe the nature of iron meteorites, it would be appropriate to present
the discovery of the Widmanstätten structure, found in nearly all iron-rich
meteorites. Widmanstätten ferrite is so intimately connected with iron
meteorites that their classification system is based on the width of the
Widmanstätten structure. However, to observe the structure, one must first cut,
polish, and etch the metal with a weak acid. The structure, which will be
explained in the next section, is composed of plates of ferrite, the body centered
cubic form of iron, occurring at characteristic angles from one another [8].

1.3.1 A Historical Introduction To Widmanstätten Ferrite In Meteorites

The Widmanstätten pattern was first observed in 1804 as William
Thomson examined the “octahedral crystalline structure that was revealed in the
iron (pallasite) etching in acid” [8]. Thomson, however, received little attention
from fellow scientists and his work was, for the most part, ignored. In that same
year, Alois von Widmanstätten, curator of the Royal Mineral Collection in
Vienna, etched a section of the Zagreb meteorite and observed the Widmanstätten
structure that since bears his name [8]. Carl von Schreibers, who worked with
Widmanstätten, published Schreibers’ Atlas of Meteorites in 1820, depicting
many etched fragments of meteorites [8]. This large gap in time for Schreibers’
publication, between 1804 and 1820, was thought to be due to the Napoleonic
wars [8]. One of the meteorites illustrated in Schreiber’s book is a direct print of
the Elbogen meteorite. Figure 1.4 represents one of the best images ever created
of Widmanstätten ferrite; it was formed by a simple application of printer’s ink to the surface of the etched sample [8].

Figure 1.4: Image of the Elbogen meteorite’s etched surface. Notice the basket-weave effect created by the Widmanstätten pattern [8].

Schreiber describes the method in which he created the ink negatives in the following excerpt:

“…the whole design can be directly printed from the surface with printer’s ink. The most elevated parts will print strongly, the less elevated ones more weakly, and the depressed ones do not print at all. Since they all alternate in an orderly way and are connected with each other, we obtain in this way not only a quite perfect and accurate reproduction of the etched surface but also a true picture of the natural structure of the mass as brought out by etching.” [8]
1.3.2 The Iron – Nickel Phase Diagram

Figure 1.5: The first published iron-nickel phase diagram, created in 1904 by Osmond and Cartaud. Recreated and adapted from [9].

In 1904, Osmond and Cartaud published the first iron-nickel phase diagram [9], which is reproduced in figure 1.5. Taenite is the meteoritic term for austenite, whilst kamacite is the meteoritic name for ferrite. Even though the Fe-Ni phase diagram has undergone many modifications over the decades, the underlying structure has remained the same (e.g., compare figure 1.5 with figure 1.6); figure 1.6 is the phase diagram that was presented by Wood in 1964 [10].
Wood’s main focus in his paper, *Cooling Rates and Parent Planets of Several Iron Meteorites*, was to create a simulation of a meteorite’s cooling rate by using the phase diagram of figure 1.6, different cooling rates, and undercoolings to match meteorites’ experimental data [10]. Wood’s phase diagram was created by combining the high temperature regions from authors Bennek and Schafmeister (1931) and the low temperature regions from authors Owen and Liu (1949) [10].
After Wood’s initial inability to match his computer-generated models to his experimental data, he realized that the ferrite was displaying much less Ni near the interface. This was caused by, a then "curious fact that attracted little attention," the Agrell effect [10]. The Agrell effect describes the variation of the $\alpha / \alpha + \gamma$ solvus at low temperatures. The slope of the solvus line is negative at elevated temperatures; however, at low temperatures the $\alpha / \alpha + \gamma$ solvus line exhibits a positive slope and the equilibrium Ni content in ferrite decreases with decreasing temperature (see figure 1.7). It was not until Wood incorporated the Agrell effect into his computer simulation and phase diagram, that he was able to perform a trial that succeeded in matching his experimental data [10].

Goldstein and Short subsequently showed that there was a decrease in Ni concentration in the ferrite, near the austenite interface. These authors observed that the $\alpha / \alpha + \gamma$ should invert back to decreasing Ni content with decreasing temperatures below approximately 450 °C, which they have incorporated into their version of the Fe-Ni phase diagram (figure 1.7) [11]. The Agrell effect has been labeled in figure 1.7 to show where the $\alpha / \alpha + \gamma$ solvus inverts.
Figure 1.7: Goldstein and Short’s binary Fe-Ni phase diagram. This phase diagram introduced the concept of the Agrell effect – the bend towards lower Ni concentration of the $\alpha/\alpha+\gamma$ solvus in temperatures below approximately 450 °C. Recreated from [11].

In 1996, Yang et al developed the currently accepted version of the binary Fe-Ni phase diagram, figure 1.8 [12]. Note that in the current version of the phase diagram, there is a monotectoid reaction (1):

$$\gamma_1 \rightarrow \gamma_2 + \alpha \quad (1)$$

at approximately 400 °C and 40 % Ni concentration; $\gamma_1$ and $\gamma_2$ are low and high nickel variants of austenite, respectively. At approximately 350 °C and at 52 % Ni, a eutectoid reaction occurs (2),
where $\gamma'$ is based on the stoichiometry of Ni$_3$Fe. Furthermore, $\gamma_2$ can order at low temperatures forming the equiatomic, FeNi, $\gamma''$ phase.

\[ \gamma_2 \rightarrow \alpha + \gamma' \] (2)

Figure 1.8: The currently accepted Fe-Ni phase diagram. $\gamma$ region represents austenite phase, $\alpha$ region represents ferrite phase, $M_s$ line represents martensite start temperature for given Ni concentration. The liquid region of the Fe-Ni phase diagram is not shown in this figure [12].

In figure 1.8, the $\gamma_1 + \gamma_2$ miscibility gap is extended below the monotectoid by the dashed lines and the extent of the spinodal is given by the hatched region. The martensite start temperature ($M_s$) is also given.
1.3.3 Formation Of Widmanstätten Ferrite

The Widmanstätten pattern develops as a two-phase mixture of ferrite ($\alpha$) and austenite ($\gamma$), the body centered cubic and face centered cubic form of iron-nickel, respectively [12]. This structure is thought to form from the nucleation and growth of ferrite in an austenite matrix as the parent body slowly cools over billions of years [12]. Widmanstätten ferrite forms at high temperatures, greater than 400 °C, and the precipitates of ferrite that originally form grow as large plate-like particles in the body of the austenite matrix. Widmanstätten ferrite nucleation and growth can be modeled by using the Fe-Ni phase diagram, a current version of which is shown in figure 1.8. Over several decades, many different theories about the formation of Widmanstätten ferrite have been postulated. The following paragraphs will develop a chronology of selected theories regarding the formation of the Widmanstätten pattern.

One of the most influential researchers in the field, John A Wood’s 1964 manuscript may be considered as the foundation for modern meteoritic study. This acknowledgment is for his work with Widmanstätten ferrite and the development of cooling rate curve models. As Wood states, “Obviously, the Widmanstätten structure formed in iron meteorites as they cooled from an initially homogeneous liquid state...and many attempts have been made to explain the structure in terms of the binary iron-nickel phase diagram” [10].

Wood’s phase diagram, shown in figure 1.6 and again in more detail in 1.9 a), contains a region of $\alpha+\gamma$ below 1000 °C, where most scientists have assumed
the Widmanstätten structure formed [10]. Current research leads us to believe that this structure formed via diffusional nucleation and growth in the solid state, as the core of the parent planet cooled through the $\alpha+\gamma$ phase field. The simplest way to explain this is as follows, best left in Wood’s words:

“Consider a large single crystal of, say, 8% Ni alloy, at a sufficiently high temperature to be in the $\gamma$ state. When it cools to below 712°C, it enters the $\alpha+\gamma$ field and under equilibrium conditions, crystals of a phase of composition $A'$,...” in Fig. (1.9 b) “..., are precipitated from the $\gamma$ alloy. The $\alpha$ crystals tend to nucleate in the form of plates, the (110) lattice planes of which are parallel to the octahedral (111) planes of the original $\gamma$ crystal, probably because this mode of transformation requires the least rearranging of the original $\gamma$ lattice” [10].
Figure 1.9: a) “Wood’s version” of the Fe-Ni phase diagram with composition profiles (b – d) at selected temperatures for an 8 % Ni alloy.  ii) the nucleation of ferrite within a single crystal austenite.  c) austenite and ferrite in equilibrium as the Ni diffuses from the ferrite to the austenite region.  d) As temperature drops austenitic diffusion slows and therefore Ni will build at the rims of the austenite. This is evidenced by the peaks of the M-profile seen in d). Adapted from [10].

As evident in the right-side illustrations of figure 1.9, ferrite (α), frequently in the Widmanstätten form, represents the low Ni phase of the Fe-Ni system. As ferrite starts to form (figure 1.9 b), Ni diffuses into the surrounding regions of retained austenite (figure 1.9 c). After a long time of α growth, a few regions of retained austenite remain, containing large concentrations of Ni approaching 60 percent (at the rim), whereas the Ni concentration in α is around 6 to 7 percent (figure 1.9 d). Although it is generally agreed that α forms in the α+γ region, the specific temperature at which Widmanstätten α will form is
controversial. There are differing opinions amongst the scientific community as to whether \( \alpha \) requires a precursor martensitic reaction, \( \alpha_2 \), to form or if it can form above the martensitic start temperature (see figure 1.8 for the martensitic start temperature). These issues are described in further detail in chapter 2.

In an alternate, but largely discredited, theory advanced by Vogel (1935, 1951), the formation of the Widmanstätten pattern was thought to develop from the melt in the high temperature (\( \delta + L \)) region, which can be seen clearly in figure 1.9 a) [10]. However, it is suggested that this delta ferrite, formed from the melt, would eventually be wholly converted to austenite during the cool through the relatively wide, single phase gamma region in binary Fe-Ni alloys. However, Vogel postulated that a high P level (0.06% min) would reduce the temperature range of the single phase austenite region and thereby promote the retention of \( \delta \)-ferrite [10]. As Wood stated, Vogel’s theory relied on the sluggishness of diffusion in a P rich system and a reduced temperature interval between the two high and low \( \alpha + \gamma \) regions for the ferritic structure to survive [10]. To test Vogel’s theory, Wood reheated and cooled both the Grant meteorite and alloys of varying compositions, comparable to the Grant meteorite examined by Vogel, in a furnace for four months cooling at a rate of 6°/day from 800 °C to room temperature and showed that any pre-existing Widmanstätten ferrite structure would be destroyed by the slow cool through the single phase austenite region. Wood showed that Ni diffused into both the center of the plessite region and the neighboring ferrite during the slow cool and that the M-profile (see figure 1.9 d) was virtually removed, i.e., the austenite was homogenized during the cooling cycle normally
experienced by a meteorite (see figure 1.10).

Figure 1.10: EPMA profiles taken by Wood in artificial alloys and iron meteorites. Profiles 1 and 2 are in 18% Ni and 8% Ni cooled alloys, respectfully. Profiles 3-5 is an 8% Ni annealed alloy. Profiles 6 and 7 were obtained from the Grant meteorite. It is clear to see the homogeneity amongst all of these samples, which exhibit no information regarding its previous discrete Ni profile [10].
Figure 1.10 c) – e) plots Ni concentration profiles from Wood’s analysis of the Grant meteorite; the M-profiles were virtually destroyed. This may be gauged by comparing figure 1.9 d) with figures 1.10 c) – e). In the former, the M-profile is characterized by a peak nickel content in excess of 30 percent whereas in the latter, the maximum nickel concentration reaches only about 12 percent. Wood suggests that it is only reasonable that the same thing would have happened in the parent body, if retained δ-ferrite were slowly cooled through the austenite region. Therefore, if Widmanstätten ferrite did form from the melt it would be destroyed during cooling in the solid state.

In 1954, Uhlig published a theory regarding the formation of Widmanstätten ferrite under high pressure. Uhlig cited evidence from previous work by Mehl and Derge that suggested that terrestrial austenitic alloys of up to 34% Ni will transform into Widmanstätten ferrite, αω, when cooled [10]. Uhlig then contrasted these laboratory studies to the idea that iron meteorites apparently do not form αω at these high Ni levels, i.e. meteorites with more than 13% Ni do not show evidence of Widmanstätten patterns to the “naked-eye”; rather they are classified as ataxites – exhibiting fine αω [10]. Uhlig advanced the idea that the Widmanstätten pattern in meteorites must have been created under extremely high pressure [10]. Uhlig proposed that 10^5 atm would shift the phase diagram enough to permit only Ni concentrations under 13% to form Widmanstätten patterns in meteoritic metal [10]. Wood however, rejects this theory since such a large pressure would require a very large parent planet. Wood explains that the cooling rate for such a planet would be too slow to cool to the appropriate temperature in
the age of the solar system [10]. Uhlig’s high pressure model requires a parent planet of 1290 km radius or greater to achieve his proposed 30000 atm, which would have more likely heated rather than cooled in the time that our solar system has been in existence [10].

The problem with Uhlig’s hypothesis is two-fold; firstly, in his analysis of information. Uhlig studied and analyzed information from the samples of Mehl and Derge [13] and Derge and Kommel [14]. According to Wood, these individuals cooled alloys of 27-34 percent Ni from the melt to room temperature over the course of a few hours and, at the time, these samples were thought to contain Widmanstätten patterns [10]. However, the structure Derge and co-workers believed to be Widmanstätten ferrite was actually martensite, which is metastable $\alpha_2$ – a distorted bcc structure. Wood demonstrated this fact by slowly cooling two alloys, one with 8% Ni and one with 18% Ni, for 4 months at a rate of 6 °C/day until they reached room temperature [10]. Wood showed that no Widmanstätten patterns had formed, but that martensite had formed along the \{111\} planes [10]. The microprobe analysis from Wood’s work is shown in figures 1.10 a) and b); the constant nickel level shows that the plate-like ferrite units formed by a diffusionless mechanism – i.e., the plates are martensitic and not Widmanstätten.

Secondly, Uhlig misunderstood the evidence from the meteoritic literature. Although the Widmanstätten pattern is no longer visible to the naked-eye above about 13 % Ni, nevertheless, Widmanstätten ferrite will form at much higher Ni levels. For example, Axon and Smith in their 1972 manuscript A Metallographic
Study of Some Iron Meteorites of High Nickel Content, reported the formation of “spindles of kamacite,” or Widmanstätten ferrite, in the San Cristobal meteorite (~25% Ni) [15]. Moreover, Axon and Smith described seven other meteoritic samples, which contained greater than 13% Ni and exhibited these same “spindles of kamacite” [15]. Although these other samples often included large inclusions, which may catalyze the precipitation of Widmanstätten ferrite, Axon and Smith’s data is conclusive evidence that Widmanstätten ferrite can form in meteorites with Ni concentrations larger than 13 percent.

As stated above, Axon and Smith refer to the Widmanstätten ferrite in their samples as “spindles” [15]. The terms spindle, needle, or acicular were coined to describe two dimensional images of three dimensional objects. As shown in section 2.3.2, what might appear to be needle-like in two dimensions is, in reality, plate-like in three dimensions.

1.4 STUDIED METEORITES’ DESCRIPTIONS

This thesis focused on the analysis of four different meteorite samples; the Cape York, Henbury, and Canyon Diablo iron meteorites and the Brenham pallasite, or stoney-iron meteorite. In the following paragraphs, a description of each of the investigated meteorite will be provided; also, an estimated time of impact, their chemical composition, and a description of microconstituents will be given.

The Cape York meteorite struck the Earth approximately 10,000 years ago in Cape York, Greenland and was found in 1894. This meteorite is in group
IIIAB; a meteoritic group refers to its chemical composition and allows scientists to tentatively group similarly composed meteorites as originating from a single parent asteroid. The Cape York meteorite is characterized by a Widmanstätten ferrite bandwidth of $1.2 \text{ mm} \pm 0.2 \text{ mm}$ and a chemical composition, according to Buchwald, of 7.84% Ni, 0.50 % Co, and 0.15% P [16]. The cooling rate of this meteorite is 3 °C per million years [11]. Our sample of the Cape York meteorite offered large “primary” ferrite plate size, chromite inclusions, swathing ferrite, “secondary” Widmanstätten ferrite, black plessite, and Neumann bands.

The Henbury meteorite struck the Earth approximately 5,000 years ago just south of Alice Springs, Australia and was found in 1931. This meteorite is also in group IIIAB and has a Widmanstätten ferrite bandwidth of $0.95 \text{ mm} \pm 0.1 \text{ mm}$. Its chemical composition, according to Buchwald, is 7.51% Ni, 0.45 % Co, and 0.09% P [16]. The cooling rate of this meteorite is 8 °C per million years [11]. Our sample of the Henbury meteorite exhibited large “primary” ferrite plate size, “secondary” Widmanstätten ferrite, fine “tertiary” Widmanstätten ferrite, black plessite, and Neumann bands.

The Canyon Diablo meteorite struck the Earth approximately 20,000 – 40,000 years ago in Winslow, Arizona and was found in 1891. This meteorite is in group IA and has a Widmanstätten ferrite bandwidth of $2.0 \text{ mm} \pm 0.5 \text{ mm}$. Its chemical composition, according to Buchwald, is 7.10% Ni, 0.46 % Co, and 0.26% P [16]. The cooling rate of this meteorite is $2 – 2.5 \text{ °C}$ per million years [11]. Our samples of the Canyon Diablo meteorite contained large ferrite size, “secondary” Widmanstätten ferrite, large and small inclusions, black plessite, and
Neumann bands.

The Brenham meteorite struck the Earth in Kiowa County, Kansas and was found in 1891. This meteorite is a pallasite, or stoney-iron, exhibiting massive inclusions and a Widmanstätten ferrite bandwidth of 0.8 mm. Its chemical composition, according to Buchwald, is 10.81% Ni, 0.55 % Co, and 0.14% P [16] and the cooling rate is 3 °C per million years [11]. Our samples of the Brenham meteorite consisted of large bands of swathing ferrite, “secondary” Widmanstätten ferrite, massive and small inclusions, and areas of black plessite.

The remainder of this thesis is devoted to a study of the nature and distribution of the ferrite phase, in the four aforementioned meteorites. In Chapter 2, a distinction between Widmanstätten ferrite and swathing ferrite will be made. In turn, Widmanstätten ferrite will be sub-divided into groups, based on size or bandwidth. It will be argued that the Widmanstätten ferrite size distribution is at least bimodal, and possibly trimodal. It will also be argued that Widmanstätten ferrite forms over a wide temperature range.

Chapter 2 also aims to clarify the taxonomic schemes that are used in describing plessite, the intimate mixture of austenite and ferrite. It is suggested that the terms “acicular ferrite” and “spindle-like ferrite” be replaced with the term secondary Widmanstätten ferrite. In addition, the use of the terms type-I plessite (Massalski et al [17]) and acicular plessite (Buchwald [16]) to describe a dispersion of secondary Widmanstätten plates in a martensitic matrix should be discontinued. Likewise, it is argued that the terms “comb and net plessite” should be replaced by (degenerate) secondary Widmanstätten ferrite.
In Chapter 3, the crystallography of the ferrite reaction is examined. It is shown, based on the work of Young in the 1920s and 1930s [18, 19], that Widmanstätten ferrite and swathing ferrite develop as separate entities with completely different crystallographic orientation relationships with respect to the parent austenite. It is also argued that it is unlikely that swathing ferrite acts as a nucleation substrate for Widmanstätten ferrite.
References:


2.1 INTRODUCTION

In this chapter, we will see that there is a hierarchy of ferrite plate/lath microstructures ranging from the very large (millimeter size) to the very small (micron size). Also, this chapter will discuss Widmanstätten ferrite, secondary Widmanstätten ferrite, swathing ferrite, Neumann bands, inclusions, and plessite, all of which are microconstituents found in meteoritic samples. Later in the chapter, we will develop an emerging hypothesis on the morphological development of Widmanstätten ferrite and compare and contrast the concepts of undercooling and delayed nucleation.

We coin the term “primary” Widmanstätten ferrite to describe the plates of millimeter order, which we believe to be the first plate-like ferrite (kamacite – meteoritic terminology) to nucleate during cooling from the single phase austenite. A second order Widmanstätten ferrite, aptly named “secondary” Widmanstätten ferrite, is thought to form at some lower temperature relative to the initial “primary” nucleation; these secondary plates may have widths on the order of 100 μm, i.e., they have grown for less time and thus have smaller size. Another form of ferrite included in the hierarchy is referred to as martensite. This body centered cubic form of ferrite is formed by shear and is the finest form of ferrite found in iron meteorites. An analysis of each form is given below in an attempt to emphasize the differences in formation temperature of each ferrite microconstituent. Finally, we describe the term “swathing ferrite” which refers to
ferrite which does not develop as a plate, and is normally associated with inclusions such as phosphides. It is argued that swathing ferrite forms prior to the nucleation of Widmanstätten ferrite, and that it is analogous to allotriomorphic ferrite, which is found in terrestrial steels.

Figures 2.1 and 2.2 are light microscopy montages, an assembly of many images to create one fully representative image, of the Cape York meteorite. In these images, large, basket-weaved Widmanstätten plates on the order of 1–2 mm are located throughout the sample. These plates are positioned 45° from the horizontal axis, and are mutually perpendicular, which allows us to conclude that the orientation of the surface is \{100\}. In figure 2.1, an unaltered montage of our Cape York meteorite sample is shown, whereas in figure 2.2 areas of interest are highlighted. Regions colored yellow display readily observable Neumann bands, evidence of shock deformation. The green features are chromite inclusions, two of which are associated with swathing ferrite (highlighted in purple). The swathing ferrite does not adopt a regular or faceted morphology, as contrasted with the primary Widmanstätten ferrite (pink), which in two dimensions is rod-like with an aspect ratio of about 25:1. The regions of enhanced brightness are given the collective term, plessite. Plessite is a complex two-phase mixture of austenite and ferrite; typically each plessite pool is surrounded by a high-nickel retained austenite, whereas the plessite interiors are duplex. Many of the plessite fields contain “black plessite” (see section 2.3.2), whilst others contain what we term secondary Widmanstätten ferrite. Examples of black plessite and secondary
yWidmanstätten ferrite are included as figures 2.3 and 2.4, but are also labeled “A” and “B” in figure 2.2, respectively.

Figure 2.1: Light microscopy montage of Cape York meteorite sample. Labels on the perimeter are for locating specific regions referred to within the text. For a more detailed analysis of this figure, compare to figure 2.2.
Figure 2.2: Light microscopy montage of Cape York sample showing highlighted areas of interest. Yellow regions represent shock deformation twins (Neumann bands), green - chromite inclusions, red - primary Widmanstätten ferrite plates1, purple - swathing ferrite, and enhanced brightness regions - plessite, which oftentimes include areas of black plessite and secondary Widmanstätten ferrite. The region arrowed A is black plessite, whereas region B represents a plessite pool containing secondary ferrite.

1 To outline all primary plates shown in figure would cover most of the screen and take away from the purpose of this image, therefore only two plates were highlighted as examples)
Figure 2.3: Light microscope montage of plessite pool containing black plessite, surrounded by a lighter gray area of high nickel retained austenite.

Figure 2.4: Light microscope montage of plessite pool containing mostly secondary Widmanstätten ferrite (e.g., at A). Black plessite is present at B.
As primary Widmanstätten plates (see figure 2.5 “A”) grow, pools of austenite (taenite – the meteoritic terminology) are, at least initially, retained and compressed into small regions (see figure 2.5 “B”). These regions can have a high concentration of Ni, which originates from the constant diffusion of Ni from the growing Widmanstätten plates. Importantly, diffusion within ferrite regions is orders of magnitude faster than in austenite – eventually leading to a buildup of Ni near the border of most retained austenite regions.

The overall Ni concentration in a given meteorite will determine the nature of its Widmanstätten pattern. For example, meteorites with less than 6 wt% Ni will be single phase ferrite and are called hexahedrites [1]; hexahedrites contain no Widmanstätten structure. Meteorites with 6 to 27 wt % Ni, contain both ferrite and austenite phases and are named either octahedrites, if they are between 6 to 16 wt % Ni or ataxites, between 11 to 27 wt % Ni [1]. In ataxites, generally the Widmanstätten pattern is only observable through a microscope (it may be argued that all ferrite is secondary Widmanstätten ferrite). However, above approximately 30 wt% Ni, the Widmanstätten pattern does not form at all. Conversely, in octahedrites a primary Widmanstätten pattern forms that can be seen with the naked eye. This is evident by the Widmanstätten plates, seen in figure 2.5, marked as “A”; notice the plate widths are on the order of 1 to 2 mm, as compared to the resolution of the eye, which is on the order of 0.1 mm.
Figure 2.5: A light microscope image of several primary Widmanstätten plates (e.g., at A). Thickening of these plates has led to the development of thin regions of retained austenite (e.g., labeled B). The impingement of two different morphological variants of the Widmanstätten ferrite has led to the creation of ferrite/ferrite grain boundaries (arrowed C) with no entrapped austenite. This impingement has led to a Widmanstätten plate morphology which has truncated ends as opposed to smoothly rounded or pointed edges. This region can be found in Figure 2.1 at coordinates (K through N, 2 through 4).

Table 2.1: Classification of Octahedrites

<table>
<thead>
<tr>
<th>Classification of Octahedrites – [1]</th>
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</thead>
<tbody>
<tr>
<td>Size Group</td>
</tr>
<tr>
<td>-------------------------------</td>
</tr>
<tr>
<td>Very Coarse</td>
</tr>
<tr>
<td>Coarse</td>
</tr>
<tr>
<td>Medium</td>
</tr>
<tr>
<td>Fine</td>
</tr>
<tr>
<td>Very Fine</td>
</tr>
</tbody>
</table>

$^2$ The bandwidth is equivalent to the average width of the plate/band of ferrite. The bandwidths quoted by e.g. Buchwald are for primary Widmanstätten ferrite only.
Octahedrites are also classified according to their primary Widmanstätten plate sizes – which range from very coarse to very fine (see table 2.1). The Cape York meteorite (see figures 2.1 and 2.2) is classified as a coarse octahedrite (see table 2.1 and figure 2.6). A classification issue among this system is that ataxites, fine octahedrites, medium octahedrites, and coarse octahedrites overlap at certain Ni concentrations.

![Iron-nickel phase diagram](image)

Figure 2.6: The iron-nickel phase diagram, which includes terminology describing meteorites of specific Ni concentrations. i.e. a medium octahedrite is an iron meteorite which contains 6.5 – 10.5 Ni wt %. Also, this figure shows the nickel percentages often found associated with ataxites and pallasites.
Meteorites may also be classified by cooling rate, which is related to its ferrite bandwidth and can be found from the “M-profile,” which develops in the retained austenite and is explained in the following section (see section 2.2). As a general rule, the faster the meteorite cools - the finer its primary Widmanstätten pattern, due to the lack of time for Widmanstätten plate growth. The Widmanstätten structure is also found in some stony-iron meteorites, which are called pallasites (see section 2.3.2).

2.2 PRIMARY WIDMANSTÄTTELN FERRITE – THE “M-PROFILE”

Figure 2.7: M-profile showing areas of Widmanstätten ferrite plates ($\alpha$) and a region of retained austenite ($\gamma$). Notice the profile of the Ni concentration takes the shape of the letter “M” from the buildup of Ni near the rim of the retained austenite.
The M-profile can be used to determine meteorites’ cooling history and therefore it is important to note the science that controls the development of the M-profile. The profile is created by the buildup of Ni near the edge of retained austenite pools. The Ni concentration in the “primary” Widmanstätten ferrite region will be low and relatively uniform, due to the high rate of nickel diffusion in ferrite. On the other hand, within the retained austenite, Ni concentrations will be high, especially in the rim region. This is due to the much slower rate of diffusion in austenite, when compared to ferrite. Accordingly, Ni concentration builds in the rim region, while austenite’s slower diffusion gradually carries Ni towards the center of the retained pool; an M-profile from the Cape York meteorite is shown in figure 2.7. This diffusion profile was obtained by plotting the Ni concentration, obtained through a microprobe line scan, as a function of the distance across an area of two Widmanstätten plates that were bisected by retained austenite.

2.3 SECONDARY WIDMANSTÄTTEN FERRITE AND PLESSITE

2.3.1 General

Austenite can be found in a wide variety of forms, oftentimes within regions of plessite. Plessite is defined as the fine-grained mixture of austenite and ferrite that forms from initially homogeneous, retained austenite regions between primary Widmanstätten plates [2]. Although the rim of retained austenite contains complex regions with a wealth of information on high temperature phase
transformations, the interior plessite region will be the area of focus in the following section. Plessite typically contains ferritic plates, in one form or another, and for this reason, it is included in this chapter regarding Widmanstätten ferrite. However, since the rim region does not contain Widmanstätten ferrite, it will not be discussed.

Figure 2.8: a) SEM mage of plessite pool in the Cape York meteorite. This image was taken from the same sample as shown in figure 2.1; this image, however, was rotated 90° relative to figure 2.1 and can be found at coordinates (C, 9). b) Increased magnification of selected area, which shows black plessite and secondary Widmanstätten ferrite. Note: The contrast in b) is inverted to show “black plessite” as black, as in a light microscope.
Figures 2.8 a) and b) are scanning election microscope (SEM) images of a plessite pool in the Cape York meteorite. Figure 2.8 a) is an image of the complete pool, whilst b) is an enlargement of the highlighted area. Note that the contrast in b) has been inverted such that the “black plessite” is indeed black, as it is in a light microscope image. A series of parallel secondary Widmanstätten plates are observed at A, whereas at D, a basket-weave of mutually orthogonal plates is present. Black plessite is arrowed B and the high nickel retained austenite rim is labeled C. Note that at e.g., A, the parallel, secondary Widmanstätten plates have impinged along much of their broad faces, creating ferrite/ferrite grain boundaries. However, discontinuous elongated films of retained austenite are still observed. At D, both face to face impingement and edge to face impingement (defined in section 2.3.2 – figures 2.14 and 2.15, respectively), together with subsequent coarsening of the entrapped austenite pools have led to a complex, duplex austenite/ferrite aggregate and a “degenerate” Widmanstätten ferrite morphology. Indeed, were it not for the observation of orthogonal plates at the periphery of D, it would be difficult to identify the reaction product as Widmanstätten ferrite. Finally, reference to the individual plates of Widmanstätten ferrite, both at A and D, show that their morphology can best be described as a double spherical cap of high aspect ratio.

2.3.2 Plessite

Plessite has been classified into specific groups by Buchwald [2] and Massalski et al [3]. Each of the plessite classifications these researchers refer to
have specific characteristics that pertain to ferritic size and shape. The following, lists various types of plessite referred to by Buchwald [2] and Massalski et al [3].

*Acicular plessite*, also known as type-I plessite according to Massalski et al [3], is comprised of “needle-like” ferrite units within black plessite (see figures 2.8 a), b), and 2.10). These ferrite units may look needle- or spindle-like [4] in the two-dimensional cross section of samples; however, in three-dimensions they are plate-like (see figure 2.9).

Figure 2.9: Schematic diagram of two-dimensional images of three dimensional objects. a) Images of a rod-like morphology are circular or elliptical. The only time a rod-like image would be observed is when the rod both intersects the surface and at a very shallow angle. b) A “needle-like” shape in two dimensions, more than likely represents a plate in three dimensions.
Figure 2.10: SEM image of “acicular” plessite (secondary Widmanstätten ferrite) and black plessite. Region analyzed from the Cape York meteorite. The “spindles” of Widmanstätten ferrite are parallel to the primary Widmanstätten ferrite plates, i.e., secondary plates A are parallel to primary plates A’ and secondary plate B is parallel to primary plate B’. This parallelism, between primary and secondary plates is also evident from figure 2.1. This further suggests a plate-like morphology of the secondary Widmanstätten ferrite.

This argument could be confirmed through the use of serial sectioning, which permits the development of a three-dimensional image of the features of interest. However, even in the absence of serial sectioning, it can be argued that the secondary Widmanstätten ferrite shown in figure 2.8 b) are two dimensional images of plates, rather than needles or spindles. If we first assume that the secondary Widmanstätten ferrite is indeed plate-like, then the two-dimensional images of figures 2.8 and 2.10 are fully consistent with the plate morphology, i.e. two-dimensional sections of a plate will always be needle or rod-like. However,
if the Widmanstätten ferrite units were assumed to be needle-like in three dimensions, then most two-dimensional sections of the needle would not yield a needle-like morphology, but rather a more equiaxed morphology (see figure 2.9a). In addition, the probability of sectioning a needle at both the right angle, and at the required position in space to produce the images shown in figures 2.8 b) and 2.10 would be very small.

Acicular plessite may be thought of as immature secondary
Widmanstätten ferrite. The connection may be established by comparing the plate orientations and morphologies of acicular ferrite to that of Widmanstätten ferrite. For example, the secondary Widmanstätten plates at A and D on figure 2.8 (and see region C.9 of 2.1) are parallel to the primary Widmanstätten plates.

The relationship between acicular, or spindle-like ferrite and primary
Widmanstätten ferrite may also be illustrated with reference to the growth of a Widmanstätten ferrite plate. If we invoke classical nucleation theory, then the shape of the ferrite nucleus will be a truncated sphere (see figure 2.11a); the sphere being capped by facets which are parallel to \(\{111\}_\gamma \parallel \{110\}_\alpha\). The aspect ratio, \(r/h\) will be given by \(r/h = \frac{\gamma_{ay}}{\gamma_{ay}^c}\), where \(\gamma_{ay}\) is the interfacial energy of the curved interfaces and \(\gamma_{ay}^c\) is the facet energy [5].

Rapid lengthening of the precipitates at rates far faster than that allowed by volume diffusion will lead to the development of a high aspect ratio plate (see figure 2.11 b); the precipitate thickens, at a much slower rate, by the ledge mechanism. It is conceivable that during the early stage of precipitate
development, the precipitate length could approach a limiting size due to soft impingement of diffusion fields. Continual thickening of the precipitate will eventually lead to a precipitate morphology which is akin to a double spherical cap (see figure 2.11 c). Later, a limiting length will be reached when hard impingement occurs, and precipitate thickening will slow due to the soft impingement with adjacent diffusional fields (see figure 2.11 d). Finally, growth may well be limited to the lateral migration of pre-existing ledges (see figure 2.11 e), which will yield a precipitate morphology similar to that of figure 2.11 f).

Primary Widmanstätten ferrite forms at a much higher temperature than secondary Widmanstätten ferrite, allowing uninhibited growth for quite a long time. However, secondary Widmanstätten ferrite grows in retained austenite pools, and therefore, is often limited in potential size (see section 2.1). The square edge, found in both “primary” and “secondary” ferrite in areas of high plate count (see figure 2.4), is further evidence that these plates form via similar mechanisms and facet from impingement. This can be contrasted to secondary plates which do not impinge other plates, which exhibit non-truncated double spherical cap morphology (see figure 2.10).
<table>
<thead>
<tr>
<th>Description</th>
<th>Schematic Morphology</th>
<th>Optical Image</th>
</tr>
</thead>
<tbody>
<tr>
<td>a) Nucleus morphology is a truncated sphere</td>
<td></td>
<td></td>
</tr>
<tr>
<td>b) Rapid lengthening leads to a precipitate of a high aspect ratio</td>
<td></td>
<td></td>
</tr>
<tr>
<td>c) Precipitate approaches a limiting length because of soft or hard impingement. Thickening occurs at a slower rate, possibly via the ledge mechanism. The macroscopic shape of the precipitate is best described as a double spherical cap. This is an “immature” ferrite plate or secondary Widmanstätten ferrite.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>d) Precipitate has reached a limiting length. Thickening is also inhibited by soft impingement. This is secondary Widmanstätten ferrite.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>e) Growth is limited to the lateral migration of pre-existing ledges.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>f) Final growth morphology of a primary Widmanstätten plate is limited by a combination of hard and soft impingement.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2.11: A schematic diagram outlining the growth of Widmanstätten ferrite from its nucleation stage (a) to its final morphology after hard impingement with another plate. Notice the sharp points in the “double spherical cap” when the precipitate is not inhibited by other growing Widmanstätten plates (b-c) as opposed to the squared edge evident in length inhibited grains (d-f).
Black Plessite [2]: Another form of plessite common in iron meteorites is type II (according to Massalski [3]), or black plessite. Black plessite, as coined by Buchwald [2], refers to plessitic regions that comprise areas of lath martensite or plate martensite appearing as discrete islands of ferrite that form via shear. The high concentration of finely dispersed islands leads to a rapid attack by etchants, leaving the area burned black after only a short encounter with weak acid [2]. The islands of martensite in this species of plessite could be considered another size-form of Widmanstätten ferrite with a band-width of 1 μm and less. An example of black plessite is shown in figure 2.3, figure 2.8 b) at “B”, and in figure 2.12.

Figure 2.12: SEM image of martensite units within black plessite. Notice that the martensite is on the order of 1 micron in size.
Comb/Net Plessite: Buchwald refers to another form of plessite he terms as comb or net plessite, which in actuality should be termed “degenerate” Widmanstätten ferrite. We coin the term degenerate Widmanstätten ferrite to describe ferrite which has impinged to such a degree, that it is barely recognizable as plate-like Widmanstätten ferrite.

Buchwald explains the relationship between comb and net plessite as “... (net plessite) is sometimes just a section perpendicular to the comb plessite” [2]. Therefore, it is easy to see why comb and net plessite are oftentimes found together within the same plessite field. The region of net/comb plessite includes small islands of austenite between the spines of what are presumably secondary Widmanstätten ferrite plates, which contain a series of parallel sub-boundaries as seen in figure 2.13. These sub-boundaries may be attributed to a polygonization process or a sympathetic process.

Figure 2.13: a) Schematic drawing of a Widmanstätten ferrite plate which is partitioned into sub-grains. b) SEM image of Widmanstätten ferrite plate with highlighted grain boundaries, where “A” denotes a grain boundary.
Figure 2.14: a) Image of comb/net plessite from the Brenham meteorite. Embedded austenite within “degenerate” ferrite is labeled “A,” whereas Widmanstätten ferrite is observed at “B” and degenerate Widmanstätten ferrite is found at “C.” b) Alternate image from Brenham meteorite showing comb/net plessite. It can be seen that much of the “degenerate” Widmanstätten ferrite still maintains a semblance of its original habit plane – marked by red lines.
Figures 2.14 a) and b) are light micrographs of what would be termed comb and net plessite by Buchwald [2]. In both instances, the comb/net plessite is comprised of ferrite units, which are either equiaxed, or elongated but with a low aspect ratio, together with islands of retained austenite; these latter islands are found either at the ferrite / ferrite grain boundaries, or within ferrite grains (e.g., at A on figures 2.14 a). The comb/net plessite is often associated with regions which can definitely be labeled as Widmanstätten ferrite (e.g., at B on figures 2.14 a and b) and sometimes is associated with regions of black plessite (D on figure 2.14 a). Therefore, do we characterize comb/net plessite as a form of degenerate Widmanstätten ferrite or as a highly tempered martensite? Evidence for the degeneration of an initially Widmanstätten microstructure is seen in both figures 2.14 a) and b) where the high aspect ratio of the original Widmanstätten plates is being lost by e.g., polygonization, which is producing a more equiaxed ferrite morphology. Remnants of the original alignment of the Widmanstätten microstructures are still evident in figures 2.14 a) and b), as shown by the red lines.

The thin films of austenite at the original Widmanstätten ferrite grain boundaries are subjected to a coarsening reaction, which will replace the films of high aspect ratio with islands of a more equiaxed morphology (see figure 2.15). Note that in figure 2.15a, face-to-face, soft impingement of the diffusion fields of the two growing Widmanstätten precipitates, and polygonization within each Widmanstätten plate, are assumed to have occurred.
Figure 2.15: a) Face-to-face soft impingement of two Widmanstätten plates. At this late stage in the ferrite reaction, it may be assumed that the volume fraction of ferrite and austenite are close to equilibrium. b) After coarsening and hard impingement, the thin austenite film has been replaced by more equiaxed pools of austenite.

The observation of intragranular austenite (figure 2.14a at “A”) can be explained as follows. Figures 2.16 a – e are schematic illustrations of the interaction between two growing Widmanstätten plates and the remnant austenite. In common with figure 2.15, it is assumed that the impingement is face-to-face. In figure 2.16a, the two Widmanstätten plates, $\alpha_a$, and $\alpha_b$ are shown as being bounded by parallel $\{111\}_\gamma \parallel \{110\}_a$ interfaces. In figure 2.16b, it is assumed that some form of shape instability occurs, which leads to pinching-off of a pool of austenite (figure 2.16c). Once a series of austenite particles have been isolated at a ferrite / ferrite grain boundary, the system is subjected to the forces for normal grain growth. Assuming that the force for grain growth outweighs the Zener drag,
exerted by the austenite particles (figure 2.16d), it is possible to embed the austenite particles in the ferrite matrix (figure 2.16e).

Figure 2.16: The creation of isolated intragranular pools of austenite (adapted from an original in Lee et al., [6], for the case of face-to-face impingement. a) Two parallel Widmanstätten ferrite plates ($\alpha_a$ and $\alpha_b$). Shape instabilities develop on the $\alpha/\gamma$ interfaces, leading to c) pinching off of the austenite to form elongated pools of austenite at a ferrite/ferrite grain boundary. d) The motion of the $\alpha_a/\alpha_b$ grain boundary into ferrite grain $\alpha_a$ is opposed by the Zener drag force. e) After impinging, the austenite pool is embedded in ferrite grain $\alpha_b$. 
Another mechanism for the formation of discrete austenite particles is shown in figure 2.17, which illustrates edge-to-face impingement. In this instance, the parallel Widmanstätten plates ($\alpha_a$) impinge on a second variant of the Widmanstätten ferrite ($\alpha_b$), creating isolated pools of austenite (figure 2.17 b).

Figure 2.17: Formation of isolated austenite pools by edge-to-face impingement. a) Three parallel Widmanstätten plates ($\alpha_a$) have impinged on each other, face-to-face. b) Hard impingement of three parallel Widmanstätten plates ($\alpha_a$), with a differently oriented plate ($\alpha_b$) creates isolated austenite pools at ferrite triple junctions.
2.4 THE CONCEPTS OF NUCLEATION, UNDERCOOLING, AND DELAYED NUCLEATION

2.4.1 Nucleation

Wood’s mechanism for the nucleation and growth of Widmanstätten ferrite may be termed the “conventional mechanism.” In essence, he assumes both diffusional nucleation and diffusional growth. Wood does not explicitly state whether undercooling is required to effect ferrite nucleation, but he does make the comment that many of the Widmanstätten plates had been subjected to supercooling prior to formation. Wood does not mention any role of a substrate in ferrite nucleation, so we may assume that Wood favored homogeneous nucleation as the mechanism of formation of Widmanstätten ferrite.

In 1984 Narayan and Goldstein discussed the nucleation of ferrite in ternary Fe-Ni-P alloys [7]. In this study, the authors examined terrestrial alloys containing 5 to 10 wt % Ni and 0 to 1 wt % P, which they later extrapolated to ferrite nucleation in meteorites. In these terrestrial experiments, both isothermal and nonisothermal heat treatments were employed in an attempt to nucleate intragranular ferrite. Five isothermal heat treatments and nine nonisothermal heat treatments were employed. In the isothermal heat treatments, samples containing 0.15 wt % P were heat treated at temperatures near 660 °C for either 350 or 700 hours and showed no evidence of intragranular ferrite; however, a sample containing 0.75 wt % P heat treated for 530 hours at 710 °C did exhibit intragranular ferrite. Narayan and Goldstein showed that ferrite precipitates did
not occur in the absence of P either intragranularly or at grain boundaries [7]. In addition, Narayan and Goldstein reported that intragranular ferrite did not form unless the matrix was supersaturated with respect to phosphorus [7].

Narayan and Goldstein concluded that in Fe-Ni-P alloys, including meteorites, “the reaction path $\gamma \rightarrow \alpha + \gamma$ for the nucleation of intragranular ferrite is not operative” [7]. Moreover, they state that there must be heterogeneous sites for nucleation within the austenite matrix. Narayan and Goldstein claim that intragranular ferrite nucleation will only occur once the alloy enters the three-phase $\alpha + \gamma + P$ field, and it cannot occur within the two-phase $\alpha + \gamma$ field.

However, their data, which might indicate that a P supersaturation is necessary for ferrite nucleation, cannot be used as a comparison for ferrite nucleation in meteorites. Although their nonisothermal samples were cooled at 5 °C/day (or 2 °C/day in one case) and the isothermal samples were held for in excess of 350 hours at temperatures within the $\alpha + \gamma$, which is quite long for terrestrial heat treatments, the fact that intragranular ferrite did not form in low P or P free terrestrial alloys is probably of limited relevance to meteorites. The difference in reaction times between these terrestrial experiments and the environment experienced in meteoritic phase transformations is of a factor of $8.2 \times 10^{10}$. This difference is enormous, and allows us to conclude with some certainty that terrestrial heat treatments cannot be usefully compared to the environment experienced during phase transformations in meteorites. It can be agreed that phosphides act as catalysts for ferrite nucleation; however these terrestrial experiments cannot be extrapolated to conclude that heterogeneous sites
of P are necessary for ferrite to precipitate in meteorites. A more complete discussion of the effect of phosphides, on the formation of ferrite, is represented in chapter 3.

Narayan and Goldstein’s argument was expanded further by Yang and Goldstein [8], who claimed that in phosphorus-rich alloys, Widmanstätten ferrite would form heterogeneously, on phosphides, immediately as the meteorite entered the three phase (α + γ + Ph) region and that in the absence of phosphides, nucleation of ferrite would not occur until the Ms temperature was reached. Hence, nucleation of Widmanstätten ferrite in phosphorous-lean alloys was postulated to occur by shear, but that growth was diffusively controlled.

2.4.2 Undercooling

It is generally agreed that αω forms in the α + γ region; however, the specific temperature at which Widmanstätten forms is still uncertain. In 1965, Goldstein and Ogilvie invoked the concept of undercooling, the necessity of a temperature decrease below the equilibrium solvus temperature before nucleation [1]. Wood also recognized that certain Widmanstätten ferrite plates were subject to supercooling and he also determined that the best fit between the calculated and experimental profiles for the Odessa meteorite combined a cooling rate with an undercooling of 80 – 120 °C.

In 1965, Goldstein and Ogilvie noted that “It is not unreasonable therefore to assume that some undercooling occurred before precipitation” and quoted the
value of 100 °C as being “not unreasonable” [1]. Depending on the model that Goldstein and Ogilvie employed, undercoolings ranging from 50 – 100 °C were estimated. It was also shown rather convincingly, that there was no unique value for the undercooling, but that different Widmanstätten plates would nucleate at different temperatures during the cooling process. For example, the authors examined the Carlton meteorite and were able to associate different diffusion profiles with different Widmanstätten plate widths and different values of the undercooling.

In 1967, Goldstein and Short reported the results of two studies on meteoritic cooling rates [9, 10], the first using nickel diffusion profiles, and the second using the Widmanstätten ferrite band width. In the first paper, the authors were able to associate asymmetric diffusion profiles with differences in undercooling and hence nucleation temperatures. In the second paper, Goldstein and Short assumed an undercooling of about 100 °C, in order to calculate meteoritic cooling rates. About a decade later, Moren and Goldstein [11, 12] reported on the cooling rate variations of Group IVA meteorites and quoted undercoolings in the range of 100 °C – 200 °C.

In 1985, Narayan and Goldstein used the “bandwidth method” for determining meteoritic cooling rates based on the data extrapolated from terrestrial experiments. The authors reported that, in the presence of phosphides, there was little evidence for any significant undercooling, but that in alloys which were not supersaturated with respect to phosphorous, then nucleation of Widmanstätten ferrite did not occur [7].
In 2006, Yang and Goldstein replaced the concept of undercooling with the idea of a nucleation temperature. For phosphorous-rich alloys, the nucleation temperature is that of the \((\alpha + \gamma + \text{Ph})\) phase boundary and the “undercooling” is set to zero [13]. Conversely, for phosphorous-lean alloys, the nucleation temperature is equated to the Ms temperature, and the undercooling is of the order of 120 °C – 150 °C [13].

### 2.4.3 Delayed Nucleation

Rasmussen introduced the concept of delayed nucleation, which takes into account the ever-changing local Ni concentration during ferrite nucleation. Initially Rasmussen ignored undercooling, but later realized that an undercooling was necessary for his model to properly describe a mechanism for ferrite nucleation. Rasmussen stated that not all ferrite nucleated at the same time, which is contradictory to Goldstein’s concept of nucleation at single temperature, e.g., Ms. Rasmussen’s assumption gives rise to varying Ni levels in the host matrix at the time of ferrite nucleation – termed bulk local Ni variation. Figure 2.18 a) – c), are schematic representations of the local bulk Ni content during ferrite nucleation.
According to Rasmussen, early nucleation occurs in an austenite matrix where the local bulk Ni content is also equal to the bulk alloy content (~ 9 wt% Ni in figure 2.18 a), whereas later nucleation will take place in Ni enriched areas which also corresponds to millions of years later and 10 – 100 degrees Celsius cooler (Figures 2.18 b and c). As stated earlier, Rasmussen initially believed that
nucleation occurred under thermodynamic equilibrium and no undercooling was necessary; however, later [18-21], he found that undercoolings were needed for his experimental modeling. Rasmussen stated that undercooling was drastically out of thermodynamic equilibrium, whereas delayed nucleation was not, or only very slightly. To compare and contrast delayed nucleation with that of Goldstein’s idea of undercooling, the following provides definitions of each author’s concepts.

- **Delayed Nucleation** – is the temperature difference between the local gamma/gamma+alpha solvus and the gamma/gamma+alpha solvus for the bulk alloy. It is assumed that the alpha nucleates at zero undercooling. (see figure 2.19 a))

- **Undercooling** – is the temperature difference between the local gamma/gamma+alpha solvus and the temperature at which the alpha nucleates. (see figure 2.19 b))
Figure 2.19: a) Schematic diagram of delayed nucleation. Delayed nucleation occurs by a shift in local Ni concentration, from the initial nucleation temperature to the next. b) Schematic diagram of undercooling. Notice that there is a finite temperature interval between the solvus line and the point of nucleation (shown by the red circle).

As stated before, Goldstein believes that all Widmanstätten ferrite formed at the same time, either when precipitation of phosphides had commenced, or at
Ms. Conversely, Rasmussen believes a stepwise nucleation occurred close to the solvus line (see figure 2.19) [14-17].

To compare the two ideas, it would be informative to analyze the thermodynamics which governs nucleation. The energy barrier to nucleation ($\Delta G^*$) for a homogeneously nucleated, non-faceted sphere is given by:

$$\Delta G^* = \frac{16\pi \gamma_{\alpha \alpha}^3}{3\Delta G_v^2},$$  \hspace{1cm} (1)

where $\Delta G_v$ is the chemical driving force and $\gamma_{\alpha \alpha}$ is the interfacial energy of the ferrite/austenite interface.

The nucleation rate ($J^*$) [18] is:

$$J^* = Z\beta^* N \exp\left(-\frac{\Delta G^*}{kT}\right) \exp\left(-\frac{\tau}{t}\right),$$  \hspace{1cm} (2)

where $Z$ is the Zeldovich non-equilibrium factor, $\beta^*$ is a frequency factor, related to the rate at which single atoms join the critical nucleus, $N$ is the number of nucleation sites/unit volume and $\tau$ is the incubation time, which may be expressed as:

$$\tau = \frac{\pi RT \tau^3}{96V_m D_{\gamma}},$$  \hspace{1cm} (3)

where $D$ is the diffusivity of Ni in austenite [19].

Even if we ignore the effect of strain energy, which effectively makes the driving force less negative, $\Delta G^*$ must tend to infinity as the temperature approaches the solvus. Hence, Yang and Goldstein’s contention that, in high phosphorus alloys, nucleation of Widmanstätten ferrite will occur at the $(\gamma + \text{Ph}) / (\alpha + \gamma + \text{Ph})$
boundary must be incorrect. Identically at this solvus point, $\Delta G_v = 0$ and $\Delta G^* = \infty$. By the same token, Rasmussen’s concept of zero undercooling, even for a nucleation delay, is infeasible.

Conversely, if we now analyze Goldstein’s theory of nucleation at $M_s$ for a low phosphorus alloy, the undercooling is now large and it appears to be rather unlikely that diffusional nucleation can be suppressed over such a wide temperature range and long time interval. The time dependent nucleation rate will only be zero precisely at the $\gamma / \gamma + \alpha$ solvus, but will be finite for any degree of undercooling. Given the vast time scales involved in the formation of the Widmanstätten pattern (one million years is equivalent to $3 \times 10^{13}$ s) and the large number of homogeneous nucleation sites ($\sim 10^{29}/m^3$), a finite nucleation rate will be obtained, even with $\Delta G^* \geq 60 \text{ kT}$.

### 2.5 SIZE DISTRIBUTIONS OF BANDWIDTHS IN IRON-NICKEL METEORITES

In the Cape York and Henbury meteorites, there are large primary Widmanstätten ferrite plates on the order of 1 to 2 mm, which weave throughout most of the sample. However, as described in section 2.3, there is at least one other, smaller, form of Widmanstätten ferrite, appropriately named secondary Widmanstätten ferrite, which forms in regions of plessite and retained austenite pools.

We may conclude that there are at least two different size orders of Widmanstätten ferrite in regard to its plate width, and it is important to
characterize the distribution of each order’s size. The results provided within this section suggest that there is at least a bimodal distribution of sizes within the meteorites studied, which may correlate with differing mechanisms for the formation of these different Widmanstätten plates, and most certainly correlate with a wide range of nucleation temperatures.

2.5.1 Cape York

The Cape York meteorite, which is portrayed in figure 2.1, has many large pools of plessite containing secondary Widmanstätten ferrite plates (see figure 2.4). Buchwald reports a bandwidth of 1.2 mm for primary Widmanstätten ferrite plates for the Cape York meteorite, which seems to be consistent with the data found for primary Widmanstätten ferrite in the present study’s size distribution (see figure 2.20). The sizes of the Widmanstätten plates, described in figure 2.20, were measured using a size-calibrated SEM and also a light microscope, which was connected to a computer and could capture pre-calibrated images. These images were then imported into ImageJ, a freely available image processor and analyzer, for size measurement, where size is accurate to a single pixel on a given image. To calculate the error involved in measuring a correct width, each plate was measured three times and the standard deviation of each was calculated. This standard deviation, which was then taken as the deviation from the true value, was then added to the width of a pixel within a given image and the summation was
divided by the average width. This method provided a percent error associated with the calculated value.

Figure 2.20: Size distribution of the bandwidths of the Widmanstätten ferrite plates in the Cape York meteorite. Notice that there is a bimodal distribution of plate widths. The larger population (with smaller size) is termed secondary
Widmanstätten ferrite, while the smaller population (with larger size) is termed primary Widmanstätten ferrite.

It has been found that the Cape York meteorite develops large Widmanstätten plates and secondary Widmanstätten plates of sizes on the order of 1500 and 50 microns, respectively, which creates a bimodal distribution of Widmanstätten ferrite plate sizes. Although the accuracy of measuring the smaller plates decreases with decreasing plate size, an average error of 16 percent in measurements of primary Widmanstätten ferrite was found. Although this error sounds significant, it would not alter the conclusion that there is (at least) a bimodal distribution of Widmanstätten ferrite plate sizes in the Cape York meteorite.
2.5.2 Henbury

Figure 2.21: Light microscope montage of Henbury meteorite. Primary Widmanstätten ferrite can be observed at A, whereas black plessite can be
observed at B. Highlighted areas are shown to emphasize the contained Widmanstätten ferrite plates of varying sizes.

The Henbury meteorite struck Earth nearly 5,000 years ago in central Australia, just south of Alice Springs. The Henbury meteorite is classified as a medium octahedrite within group-IIIAB iron meteorites and displays a primary Widmanstätten ferrite average bandwidth of 0.9 mm, labeled “A” in figure 2.21. Secondary Widmanstätten ferrite is found in many of the larger plessite fields (e.g., at C on figure 2.21) and what may be termed “tertiary” Widmanstätten ferrite is found in association with small pools of black plessite (e.g. at B on figure 2.2.1). Examples of secondary and “tertiary” Widmanstätten ferrite are shown in the highlighted regions and the associated SEM images.

This high number density of secondary and tertiary Widmanstätten ferrite has led to a trimodal size distribution of Widmanstätten plate bandwidths (see figure 2.22). In figure 2.22, the x axis has been created using a logarithmic scale due to the large distribution of bin sizes, without which the size distribution would not fit on a reasonably sized graph. The bin size used for the “tertiary” Widmanstätten ferrite was on the order of 0.1 micron, whereas the primary Widmanstätten ferrite required a bin size increment of 100 microns. The reasons for such a large change in bin size are straightforward, if for example we choose a large bin size, the tertiary field would turn to a delta function and a complete loss of definition between points would result. If, on the other hand, a constant, small bin size were used, the figure would be incredibly wide, losing the resolution of the primary Widmanstätten ferrite and the ability to incorporate it into a document.
Figure 2.22: Size distribution of Widmanstätten ferrite plate bandwidths in the Henbury meteorite. Notice that there is a trimodal distribution of plate widths. The larger population represents ternary Widmanstätten ferrite, the middle population represents secondary Widmanstätten ferrite, and the small population represents primary Widmanstätten ferrite.
I have included an error bar into figure 2.22 to represent the human error and image pixel limitations, which are explained in the previous section. As one can see, the consideration of this error within the size distribution does not alter the conclusion of a multimodal size distribution within the Henbury meteorite.

2.6 RESULTS OF MICROPROBE STUDIES

In an attempt to better understand the Ni profiles within plessite pools and the temperature (time) of nucleation of secondary Widmanstätten plates, it was of import to use electron probe micro analysis, EMPA, on plessite regions within the Cape York meteorite. The goal of this experiment was to employ the most recent Fe-Ni phase diagram and local Ni concentrations from EPMA data to extract information regarding the earliest possible time of nucleation for specific Widmanstätten ferrite plates.
The currently accepted Fe-Ni phase diagram of Yang et al, [20], was analyzed by DataThief allowing for the extraction of an Ni-dependent equation for the $\gamma / \alpha+\gamma$ solvus line and $M_s$ line; these equations are shown in figure 2.23 and the former is listed here:

\[ y = -0.0018x^3 + 0.2472x^2 - 20.598x + 883.09 \]  \hspace{1cm} (4)

where $y$ is the temperature of nucleation and $x$ is the local Ni concentration. The $\gamma/\alpha+\gamma$ solvus line equation would then allow us to calculate the last possible temperature at which ferrite cannot form as an alloy is cooling through the single $\gamma$ phase across the $\gamma/\gamma+\alpha$ solvus.
Local nickel concentrations were measured using a method similar to that outlined by Rasmussen [14-17], by averaging concentrations of Ni through plessite and its secondary ferrite plates. For example, the known average Ni level of the Cape York meteorite, according to Buchwald is 7.84 % [2], which corresponds to a temperature of 735 °C for primary Widmanstätten ferrite nucleation. This corresponds to the vertical red line in figure 2.23.

Figure 2.24 is an SEM montage of a region of plessite. In this region, we see a wide plessite pool, on the order of 250 microns, containing small, secondary Widmanstätten ferrite plates. The four red lines represent EPMA lines scans. The resulting data was plotted outlining the change in Ni concentration across the length (or width) of different plates. Figure 2.25a is the microprobe trace along the length of the plessite pool (i.e., trace 1 on figure 2.24). Notice that the diffusion profiles from adjacent secondary Widmanstätten plates, a – d, do not overlap each other. However, the “bulk” Ni concentration is about 14 – 15%, a level that was set prior to the nucleation of the secondary plates, by the primary Widmanstätten ferrite plates. Figure 2.25b is the composition profile across plate b (figure 2.25a), it may be seen that the width of the diffusion profile in the austenite is less than 10 microns. Restated, in the time interval during which secondary plate “b” was growing, the diffusion distance in the austenite is somewhat less than 10 microns. Because the width of the plessite field is in excess of 100 microns, we can confidently assume that the measured “bulk” level of 13.8 % Ni was established at the time of nucleation of the secondary plates and
was not significantly changed by growth of the primary Widmanstätten ferrite, subsequent to nucleation of the secondary plate.

Figure 2.24: Plessite pool containing several small Widmanstätten ferrite plates on the order of 20 microns in width. Four separate microprobe traces were conducted within this plessite region; these regions are highlighted and numbered in red.
Figure 2.25a: Ni concentration profile along the length of the plessite pool obtained via microprobe analysis. This total image corresponds to red trace “1” in figure 2.24. The Ni concentration slowly drops overall. This is due to the increased width of the plessitic region; hence, less Ni could diffuse into the center of the pool. The Widmanstätten plates, labeled a-g, are referred to in table 2.2, where the local bulk Ni concentration and maximum temperature of nucleation is given.

Figure 2.25b: Ni concentration profile associated with plate “b” in figure 2.25a. Note, the width of the diffusion profile in the austenite is less than 10 microns.
In a wide plessite pool, where the Ni diffusion fields of the secondary Widmanstätten ferrite plates do not overlap (as in figure 2.24), the local bulk Ni content for the successive, secondary Widmanstätten ferrite nucleation can be determined. The maximum temperature of secondary Widmanstätten ferrite nucleation can be calculated by determining the local bulk nickel Ni concentration, through the use of EPMA, and equation (4). To be precise, the temperature found is, in actuality, the last temperature at which ferrite could not form during the meteorites’ cool. The surrounding local bulk Ni concentration and temperature for which these plates could have nucleated is summarized in table 2.1, where “plate a” corresponds to “plate a” in figure 2.25.

Table 2.2

<table>
<thead>
<tr>
<th>Plate (as in figure 2.25)</th>
<th>Local Bulk Nickel Concentration (wt %)</th>
<th>Calculated Temperature of Nucleation(^3)</th>
<th>Calculated Temperature of M(_{s})</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>13.8</td>
<td>634 °C</td>
<td>420°C</td>
</tr>
<tr>
<td>b</td>
<td>13.6</td>
<td>641 °C</td>
<td>425°C</td>
</tr>
<tr>
<td>c</td>
<td>13.4</td>
<td>644 °C</td>
<td>430°C</td>
</tr>
<tr>
<td>d</td>
<td>13</td>
<td>647 °C</td>
<td>440°C</td>
</tr>
<tr>
<td>e</td>
<td>12.7</td>
<td>653 °C</td>
<td>448°C</td>
</tr>
<tr>
<td>f</td>
<td>12.3</td>
<td>658 °C</td>
<td>459°C</td>
</tr>
<tr>
<td>g</td>
<td>12.0</td>
<td>664 °C</td>
<td>467°C</td>
</tr>
</tbody>
</table>

\(^3\) The “calculated temperature of nucleation” refers to the last possible temperature in which ferrite could not form, therefore any degree of temperature cooler than the value listed in table 2.2 would serve to be the first temperature of possible nucleation. The concentrations and nucleation temperatures have been rounded to three significant digits; this is to show that there is inherent ambiguity and error within the calculations. This is to serve as an approximate value of nucleation only.
However, if the plate lies within the plessite pool’s Ni diffusion field, integration of Ni concentration by distance within the particular plate’s diffusion field must be performed (see figure 2.24 trace “2” and figures 2.26a and b).

Therefore, to calculate the Ni concentration and temperature for nucleation of plate 2, we must interpolate the original composition of the plessite profile. This process can be completed by overlaying the left half of the profile onto the right, since the plessite profile was symmetrical before secondary Widmanstätten ferrite nucleation. Using this method, the plate had nucleated in a Ni concentration of 18.7 %, which correlates to a temperature of 573 °C.

![Ni concentration vs x distance](image)

Figure 2.26a: Microprobe analysis of trace “2” of figure 2.24. Notice the high nickel spike in the diffusion zone outlining the plate of Widmanstätten ferrite. Therefore, we technically see two very asymmetric M-profiles next to each other, rather than symmetric M-profiles such as seen in figure 2.5. In the center of the profile, the data exhibits considerable scatter; this can be attributed to a field of martensite in the center of the plessite region.
Figure 2.26b: Expanded profile of interior ferrite region shown in figure 2.26a; this image allows for the accurate determination of diffusion fields in reference to the original Ni concentration.

Figure 2.27: Microprobe analysis of trace “3” of figure 2.24. The abnormally low nickel values within the Widmanstätten plate correspond to ferrite/ferrite subgrain boundaries. The high nickel regions of this figure can be attributed to surrounding austenite surrounding the Widmanstätten ferrite plate, this region can be found in figure 2.24.
Figure 2.25 is a microprobe trace along the length of the secondary Widmanstätten plate marked “3” on figure 2.24. The M-profiles in the austenite are highly asymmetric because they are comprised of the diffusion fields from the neighboring primary Widmanstätten ferrite and the diffusion profile from the tips of the growing secondary Widmanstätten plate; the former are relatively wide whilst the latter are rather narrow. Within the secondary Widmanstätten plate itself, there are variations in nickel concentration; these variations correspond to minima in nickel levels at ferrite / ferrite sub-boundaries. It is postulated that the nickel at a ferrite grain boundary can equilibrate with the austenite, to a lower temperature than that in the body of the Widmanstätten plate, because of a rapid diffusivity in the former as compared with the latter. According to Porter and Easterling [5], if we take the Zener approach on precipitate growth, we can estimate the growth rate across the thickness of the plate is as follows:

\[ V = \frac{dx}{dt} = \frac{D(\Delta C_\alpha)^2}{2(C_\alpha - C_\gamma)(C_\alpha - C_0)x} \]

(5)

where \( V \) is the growth rate, \( C_\alpha \) is the precipitate composition, \( C_0 \) is the bulk concentration, \( D \) is the interdiffusion coefficient, \( C_\gamma \) is the solute composition, and \( x \) is the thickness of the precipitate plate [5]. As one can see, equation (1) can further reduce to (2):

\[ V \approx \frac{1}{x} \]

(6)

and therefore, growth in this direction slows with time.
Diffusion controlled lengthening of the plate is controlled by the Gibbs-Thomson effect, which raises equilibrium conditions within the matrix at the precipitate edge to $C_R$ [5]. The growth rate $V$ is now equal to (3):

$$V = \frac{D}{(C_\alpha - C_R) kr} \Delta C$$  \hspace{1cm} (7)

where $V$ is the growth rate, $C_\alpha$ is the precipitate composition, $\Delta C = C_0 - C_R$, $D$ is the interdiffusion coefficient, $k$ is a constant, and $r$ is the tip radius. As one can see, equation (3) can further reduce to (4):

$$V \approx \frac{1}{r},$$  \hspace{1cm} (8)

where $r << x$. Therefore, growth is constant, but much faster in this direction [5].

Hence, the asymmetric profiles of figure 2.27 are comprised of long range diffusion profiles, associated with the thickening of the primary Widmanstätten ferrite, and a relatively short range diffusion field that is associated with the lengthening of the secondary Widmanstätten ferrite. This argument can again be applied to figure 2.24 trace “4,” where the trace again follows the length of a Widmanstätten ferrite plate. As shown in figure 2.28a, one would expect to see asymmetric M-profiles, which are evident on each side of the Widmanstätten ferrite plate. This is due to the short diffusion field from the tips of the secondary Widmanstätten plate intersecting the original diffusion field of the primary Widmanstätten ferrite plates within the plessite (see figure 2.28b).
Figure 2.28a: Microprobe analysis of trace “4” of figure 2.24. The abnormally low nickel values at a, b, and c correspond to ferrite/ferrite sub-grain boundaries, which are arrowed on the image at the bottom of the figure.

Figure 2.28b: Expanded profile of interior ferrite region’s left diffusion field shown in figure 2.28a; this image allows for the accurate determination of diffusion fields in reference along the length of the plate.

Using the same methodology as outlined in figure 2.25, an equation for the alpha/alpha+gamma solvus can be obtained, allowing for the temperature
calculation at which sub-grain boundaries within plates of Widmanstätten ferrite equilibrate with the adjacent austenite, as shown in figure 2.28. The equation for the alpha / alpha+gamma solvus is listed here:

\[ y = 4.1872x^5 - 78.945x^4 + 588.62x^3 - 2157.5x^2 + 3916.2x - 2620.5 \]  

(9)

where \( y \) is the temperature of nucleation and \( x \) is the local Ni concentration. Since it is known that the ferrite can equilibrate at temperatures below the temperature at which the maximum nickel concentration in ferrite occurs, equation (9) represents the curve fit to the lower portion of the alpha / alpha+gamma solvus.

Table 2.3 lists the nickel concentrations and the temperatures at which the sub-boundaries in the ferrite equilibrated with the adjacent austenite.

Table 2.3

<table>
<thead>
<tr>
<th>Sub-grain (as related to figure 2.28)</th>
<th>Local Bulk Nickel Concentration (wt %)</th>
<th>Calculated Temperature of Equilibrium⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>4.7</td>
<td>330 °C</td>
</tr>
<tr>
<td>b</td>
<td>4.3</td>
<td>292 °C</td>
</tr>
<tr>
<td>c</td>
<td>4.5</td>
<td>305°C</td>
</tr>
</tbody>
</table>

In table 2.4, the equations in figure 2.23 have been used to calculate a series of maximum nucleation temperatures for primary and secondary Widmanstätten ferrite, as well as martensite, for the Cape York meteorite. The

⁴ The “calculated temperature of equilibrium” with regards to the sub-grain boundary formation refers to the temperature in which the sub-grain boundaries could equilibrate. These values were found by correlating the Ni concentration in figure 2.28 to the temperature of the alpha/alpha+gamma solvus.
values in this table represent the maximum temperatures at which nucleation could occur for specific ferritic plates; however, it should be mentioned that the temperature of nucleation varies with the Ni concentration and hence the values given in this table are only approximate.

Table 2.4

<table>
<thead>
<tr>
<th>Microconstituent</th>
<th>Local Nickel Concentration (wt %)</th>
<th>Calculated Temperature of Nucleation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Widmanstätten Ferrite (γ / γ+α equation)</td>
<td>7.84</td>
<td>735 °C</td>
</tr>
<tr>
<td>Secondary Widmanstätten Ferrite (γ / γ+α equation)</td>
<td>13.3</td>
<td>649 °C</td>
</tr>
<tr>
<td>Martensite (Mₙ equation)</td>
<td>13.0</td>
<td>440 °C</td>
</tr>
</tbody>
</table>

In section 2.5, we discussed the possibility of multimodal Widmanstätten ferrite nucleation bursts. Further evidence supporting this argument comes from a comparison of the diffusion profiles of both primary Widmanstätten ferrite and secondary Widmanstätten ferrite. Using the microprobe data presented in section 2.6, we can conclude that the two variants must have nucleated at different temperatures.

In the case of primary Widmanstätten ferrite, we can estimate from figures 2.7 and 2.26, that the width of the Ni diffusion profile is at least 100 microns; noting that the Ni diffusion fields overlap in the center of a 200 micron plessite pool. For the secondary Widmanstätten ferrite, the width of the Ni
diffusion profile in figure 2.25 is approximately 15 – 20 microns. A comparison of the Ni diffusion widths is given in table 2.5.

Table 2.5

<table>
<thead>
<tr>
<th>Microconstituent</th>
<th>Width of Diffusion Profile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Primary Widmanstätten Ferrite</td>
<td>&gt; 100 microns</td>
</tr>
<tr>
<td>Secondary Widmanstätten Ferrite</td>
<td>15 - 20 microns</td>
</tr>
</tbody>
</table>

2.7 SWATHING FERRITE

This section is devoted to the description of swathing ferrite in iron-nickel meteorites and pallasites. Considering the association of swathing ferrite with inclusions within meteorites, much of this discussion will focus on swathing ferrite within meteoritic samples which bear large inclusions, such as the Canyon Diablo, Brenham, and Cape York meteorites.

At this point, it is worthwhile to introduce some terminology. In the meteoritic literature, the ferrite that envelops e.g., schreibersite is termed “swathing” ferrite. In the steel literature, the term allotriomorphic is applied to precipitates which have an ill-defined shape. We will use the two terms interchangeably, in that swathing ferrite is without any defining shape; it is allotriomorphic.

Frequently meteorites such as the Brenham and Canyon Diablo, contain schreibersite (an iron-nickel phosphide), which according to Young, is always
surrounded by an allotriomorphic, or swathing, ferrite [21]. Axon and Smith
(1972), suggested that swathing ferrite forms from these massive inclusions
within the austenite parent [4].

In 1939, Young described swathing ferrite as ferrite that exhibited a non-
Widmanstätten ferrite morphology; specifically, he described it as a ferrite, which
in contrast with Widmanstätten ferrite, did not fall within 9° of the Kurdjumov-
Sachs or Nishiyama-Wasserman orientation relationship [21]. Furthermore
through the use of an inverse pole diagram, Young showed a strong orientation
maximum not belonging to the Widmanstätten-type of orientation and was able to
confidently attribute this maximum to swathing ferrite, due to the high phosphide
concentration of the meteorite studied [21]. His experimentation and findings will
be further discussed in Chapter 3.

In 1978, Clarke and Goldstein described four forms of phosphide
inclusions, namely massive schreibersite, rhabdites, grain boundary schreibersite,
and micro-rhabdites. Clark and Goldstein explained that the growth of massive
schreibersite precipitates begins at around 850 °C, producing large volumes of
phosphorus-depleted austenite. Further reductions in P levels occurred by the
subsequent precipitation of much smaller phosphides, called rhabdites, below 600
°C. These inclusions are significantly different from that of schreibersite where
rhabdites form in the ferrite and schreibersite forms in austenite.

Clarke and Goldstein also describe a third type of schreibersite inclusion;
grain boundary schreibersite, which they found to form at the pre-existing
swathing ferrite-austenite boundary. According to Clarke and Goldstein, this
replacement of the boundary with areas of schreibersite is then followed by the nucleation of Widmanstätten ferrite within the remainder of the meteorite, which they state occurs by 600 °C [22]. The last form of inclusions referenced by Clarke and Goldstein, were homogeneously nucleated micro-rhabdites. The differentiation between micro-rhabdites and rhabdites, besides the size difference, is not clearly defined by Clarke and Goldstein; however, the authors stated that these latter inclusions nucleated at approximately 400 °C [22].

According to Goldberg et al [23], swathing ferrite was not limited to nucleation at schreibersite inclusions; they show evidence that wide swathing ferrite also outlined troilite, an iron sulfide. Although it seems that schreibersite tends to nucleate ferrite, of the swathing type, it is also apparent that swathing ferrite borders a multitude of inclusions found in meteorites. For example, the current work has proof of swathing ferrite in contact with olivine, a magnesium-iron silicate, inclusions as well as a chromite, or iron-chromium oxide, inclusion (see figure 2.31 and 2.32). This suggests that schreibersite is no more successful at nucleating ferrite than many other meteoritic inclusions.
Figure 2.29: Montage of the Canyon Diablo meteorite sample surface. Notice large schreibersite inclusions as well as a highlighted region of secondary Widmanstätten ferrite located within a plessite region. This region is associated to the SEM image at left, where the Widmanstätten ferrite plates are visible.

In the Canyon Diablo meteorite, the present study has found both massive schreibersite inclusions and rhabdites, shown in figures 2.29 and 2.30, respectively. Figure 2.29 is a montage of a Canyon Diablo meteoritic sample which was deliberately chosen because of the large inclusion, which bisects the image. This region consists primarily of swathing ferrite, which borders the large schreibersite inclusion. However there is also evidence of secondary
Widmanstätten ferrite, located within small plessite pools. In addition, the upper region of this meteoritic sample contains what could arguably be two primary Widmanstätten ferrite plates (arrowed).

![Image of small rhabdites, located within the large ferrite matrix of the Canyon Diablo meteorite.](image)

Figure 2.30: Image of small rhabdites, located within the large ferrite matrix of the Canyon Diablo meteorite.

In the Cape York meteorite, there is evidence of swathing ferrite, which again borders an inclusion; however, in this case it is not the phosphide schreibersite. In the Cape York meteorite, it is chromite, an iron-chromium oxide. As seen in figure 2.31, the swathing ferrite (shown as “A”), which surrounds the chromite inclusion (found in N-6 to R-14 of figure 2.1 or as “C” in figure 2.31) is
not parallel to other Widmanstätten ferrite plates (shown as “B” in figure 2.31) within the montage.

Figure 2.31: Image depicting chromite inclusion (C) outlined by swathing ferrite (A). Notice that the swathing ferrite does not exhibit long range parallel plates as often found in Widmanstätten ferrite or an orientation similar to that of Widmanstätten ferrite (B).

Figure 2.32 is an image of the Brenham pallasite, a stoney-iron meteorite; olivine and schreibersite inclusions, and large pools of swathing ferrite are observed. This sample contains a large metallic region, which is book-ended by inclusions. The metallic region consists of a large border of swathing ferrite, shown in figure 2.32 by a red border. This region encapsulates a large, plessite region consisting primarily of secondary Widmanstätten ferrite and black plessite (see section 2.3.2).
Figure 2.32: Montage of the Brenham pallasite. Notice the large bands of swathing ferrite that envelop the central plessite pool. The swathing ferrite is outlined in red, whereas the plessite pool is outlined by swathing ferrite.

As stated earlier, swathing ferrite can be found outlining a number of inclusions, such as schreibersite, troilite, olivine, and chromite. In figure 2.33, and a second sample from the Brenham meteorite, there is evidence of massive troilite, olivine, and schreibersite inclusions, which frame large (approximately 1 – 2 mm in width) bands of swathing ferrite.
Figure 2.33: Montage of alternate sample of Brenham meteorite. In this image we can see that there are three different inclusions, which are bordered by swathing ferrite. Again we see a large area of plessite, which contains Widmanstätten ferrite and black plessite.

An important observation made by Clarke and Goldstein is that areas containing a well-developed Widmanstätten pattern are well away from large schreibersite inclusions. In all cases of the current authors’ research, this observation has been confirmed. In the sample of the Cape York meteorite, there is one, long chromite inclusion which leads to the development of one band of
swathing ferrite (see figure 2.31). On the other hand, in the Canyon Diablo meteorite, which offers many, large phosphide inclusions we see evidence of nearly all swathing ferrite (see figure 2.29). There is evidence of few, small Widmanstätten ferrite plates within plessite fields, but for the most part the sample is composed of swathing ferrite.

Figure 2.34: Image of the Santa Luzia meteorite sample analyzed by Clarke and Goldstein in 1978. In this image it is evident that regions containing swathing ferrite do not contain Widmanstätten ferrite and regions containing Widmanstätten ferrite do not show evidence of swathing ferrite. This is further evidence for the dissimilarity of the two microconstituents. From [22].
In the Santa Luzia meteorite, analyzed by Clarke and Goldstein, areas of swathing ferrite completely border each of the inclusions, whereas the Widmanstätten ferrite is located in regions far from the inclusions (see figure 2.34).

As Buchwald states in his 1977 manuscript, “When upon primary cooling the high-temperature austenite (taenite) phase became unstable, the transformation to ferrite (kamacite) took place heterogeneously upon inclusions, so that these became enveloped in 'swathing kamacite'. Away from the inclusions, however, the transformation had to occur homogeneously, which resulted in the well-known Widmanstätten structure” [24]. It may be concluded with some certainty that the nucleation of Widmanstätten ferrite and swathing ferrite are competing processes, i.e. if there is evidence of one form, there is often a lack of evidence of the other.

Further discussion on swathing ferrite and its connection to Widmanstätten ferrite will be developed in Chapter 3. The possibility of Widmanstätten ferrite nucleation from an allotriomorphic, or swathing ferrite, host will be presented and a subsequent discussion on the orientation relationships between austenite and ferrite and the misorientations between and within grains of allotriomorphic and Widmanstätten ferrite will be offered.

2.8 SUMMARY

This section provides a brief summary of the major findings of the chapter; a more lengthy discussion of the implications of these findings is
presented in Chapter 4. There are three types of ferritic transformation product. These are swathing ferrite (e.g., see figure 2.33), Widmanstätten ferrite (e.g., see figure 2.1), and martensite (e.g., see figure 2.12). It would appear that swathing ferrite is located exclusively at non-metallic inclusions and is probably the first ferrite to form as the meteorite cools. For example, reference to figure 2.33 shows that the width of the swathing ferrite is about one mm, whereas the bandwidth of the Widmanstätten ferrite is 0.2 mm and less. Widmanstätten ferrite would appear to form independently of an inclusion and is never found in intimate association with e.g., massive schreiversite. The Widmanstätten ferrite displays a wide range of bandwidths, spanning three orders of magnitude (see figures 2.20 and 2.22). In addition, the widths of the diffusion profiles which are associated with Widmanstätten ferrite vary by an order of magnitude (compare figure 2.7 with figure 2.28). These observations, at the very least, require that Widmanstätten ferrite forms over a wide temperature range. Finally, we have argued that current terminology regarding needle or spindle-like ferrite, and comb/net plessite should be retired and replaced by the terms secondary Widmanstätten ferrite and degenerate Widmanstätten ferrite.
References:


CHAPTER 3: THE CRYSTALLOGRAPHY OF WIDMANSTATTEN FERRITE

3.1 INTRODUCTION

The objectives of this chapter are to present a coherent, historical description of the crystallography of Widmanstätten ferrite in iron-nickel meteorites and steels, and to explain the relationship between Widmanstätten ferrite and swathing ferrite (in meteorites), and between Widmanstätten ferrite and allotriomorphic ferrite (in steels). This chapter begins by describing one of the more seminal crystallography studies of the Widmanstätten ferrite reaction, that of Young in 1926 and 1939 [1, 2]. Young was able to establish both the orientation relationship between austenite and Widmanstätten ferrite, and the habit plane of the Widmanstätten plate. Young was also able to make some very prescient statements about the orientation of what is called swathing ferrite.

Images of Widmanstätten ferrite have already been presented in figure 2.5 “A” and an image of swathing ferrite is given in figure 2.32 (outlined in red).

The chapter concludes by examining the relationship between Widmanstätten ferrite and swathing ferrite in the Brenham pallasite. It will be strongly argued that the swathing ferrite forms prior to the Widmanstätten ferrite, but does not act as a nucleation substrate, i.e. Widmanstätten ferrite does not form by sympathetic nucleation, but must evolve independently from the swathing ferrite.

As stated in sections 2.1 and 2.4.1, ferrite forms as large plate-like
precipitates in the body of the austenite matrix. However, this precipitation of ferrite plates is not crystallographically random. Nucleation and growth occurs at specific orientations with respect to the austenite lattice [3]. As shown in the following, the orientation of Widmanstätten ferrite happens to be octahedral, precipitating on the \{111\} austenite planes [3]. Images of specific orientations of Widmanstätten ferrite, albeit in a carbon steel, are shown in figure 3.1.

![Figure 3.1: Three separate orientations of Widmanstätten ferrite (the areas in white) in a hypoeutectoid steel. From these images we can determine that Widmanstätten ferrite grows on a habit plane of \{111\}. Orientations of surface normal’s from left to right are: (001), (111), and (110) [3].](image)

### 3.2 METEORITIC CRYSTALLOGRAPHY: THE YOUNG PAPERS

To the author’s knowledge, the first individual to study the habit planes and orientation relationships of Widmanstätten ferrite in meteorites was J. A. Young. Young, in his 1926 manuscript, used x-ray diffraction to examine the crystallography of the Widmanstätten ferrite reaction [1]. Young further studied the habit plane of Widmanstätten ferrite by creating a section parallel to one of the faces of the octahedral plates. Young subsequently obtained x-ray diffraction data
from Widmanstätten plates that were parallel to this sectioning plane. This enabled him to determine the crystallographic indices of the habit plane. Young also obtained x-ray data from Widmanstätten plates that were orthogonal to the sectioning surface. This latter experiment allowed him to examine the matching of trace directions within the habit plane. If sectioning parallel to a face of the octahedron, one will see plates which meet to form an equilateral triangle and also plates which lie parallel to the surface, as can be seen in figure 3.2 [1].

![Diagram of Widmanstätten plates](image)

Figure 3.2: Sectioning of octahedral plane of Widmanstätten ferrite parallel to one of the faces of the octahedron. This will produce three of the habit planes at 60° from one another and one plate parallel to sectioning plane.

Young was able, through the use of his x-ray reflections, to show that $(110)_\alpha$ was closely parallel to $(111)_\gamma$ and that the habit plane was parallel to $(111)_\gamma \parallel (110)_\alpha$. Young also demonstrated that, within the parallel $(111)_\gamma \parallel (110)_\alpha$ habit
plane, the trace directions of low index planes were close to, but not exactly, parallel (see figure 3.3).

![Diagram]

**Figure 3.3:** Young’s data for the Canyon Diablo meteorite, expressed as the deviation of the experimentally determined orientation relationship from the Nishiya-Wasserman (N-W) orientation relationship (O.R.). $\varphi$ is the angle between the nominally parallel $(111)_\gamma \parallel (110)_\alpha$ planes, whereas $\theta$ is the angle between the [001] and [110] directions (see figure 3.5). A value of $\theta = 0$ corresponds to the N-W O.R. whereas $\theta = 5.25^\circ$ corresponds to the Kurdjumov-Sachs (K-S O.R.). The data show that neither the K-S, nor the N-W O.R.s are precisely obeyed.

Young expressed the ferrite to austenite orientation relationships before the Kurdjumov-Sachs (K-S) or Nishiya-Wasserman (N-W) papers were published in the 1930s; perhaps the K-S O.R. should be named the Young-Kurdjumov-Sachs orientation relationship.
In 1939, Young accurately measured the crystallography of the Widmanstätten ferrite by cutting three orthogonal sections of his meteoritic sample. He started by cutting, polishing, and etching a sample of the Canon Diablo meteorite and subsequently cut two more mutually orthogonal slices from the sample. This permitted for accurate measurements of the angles between the Widmanstätten plates. An image of Young’s sectioning can be seen in figure 3.4.

![Figure 3.4: Young’s method to accurately find angles between the four Widmanstätten plates orientations (1-4) in the Canyon Diablo meteorite. Redrawn from [2]. Young compared his data with the known tetrahedral angle of 109.5 degrees. This latter information is presented in table 1.2.](image)

By tracing the various $\gamma/\alpha$ interfaces (1-4 on Figure 3.4) from one section to another, Young was able to unambiguously orient the Widmanstätten plates. Young compared his experimental data with the theoretical tetrahedral angle of...
109.5°, the comparison is shown in table 3.1, where “plate” refers to the plates of figure 3.4.

Table 3.1: The Tetrahedral Angle Comparison

<table>
<thead>
<tr>
<th>Meteorite</th>
<th>Tetrahedral Angle</th>
<th>Plate 1 - 2 Angle</th>
<th>Plate 1 - 3 Angle</th>
<th>Plate 1 - 4 Angle</th>
<th>Plate 2 - 3 Angle</th>
<th>Plate 2 - 4 Angle</th>
<th>Plate 3 - 4 Angle</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Canyon Diablo</td>
<td>109.5</td>
<td>105.6</td>
<td>110.9</td>
<td>110.6</td>
<td>109.9</td>
<td>113.2</td>
<td>107.3</td>
<td>2.721</td>
</tr>
<tr>
<td>Butler</td>
<td>109.5</td>
<td>108.2</td>
<td>110.6</td>
<td>107.9</td>
<td>111.1</td>
<td>109</td>
<td>110.7</td>
<td>1.391</td>
</tr>
<tr>
<td>Carlton</td>
<td>109.5</td>
<td>107.5</td>
<td>108.5</td>
<td>107.3</td>
<td>110</td>
<td>110.5</td>
<td>112.8</td>
<td>2.095</td>
</tr>
</tbody>
</table>

As may be seen from table 3.1, the measured angles between the four Widmanstätten planes all approximate to the tetrahedral angle. Therefore, one may assume with some certainty that the habit plane of the Widmanstätten ferrite is \{111\}_\gamma.

Young’s major conclusions of his series of papers are as follows:

1. \{111\}_\gamma is parallel to an octahedral plane of the Widmanstätten ferrite (see table 3.1) [2].

2. \{110\}_a is parallel to the octahedral plane of the Widmanstätten structure and is thus parallel to the \{111\} of the austenite [2].

3. The [001] ferrite direction, which lies in the \{110\} habit plane, makes a small angle (less than 8°) with one of the \{111\}_\gamma directions which lies in the habit plane [2] (see figures 3.3 and 3.5).

Young takes this information and superimposes two families of planes (\{110\}_a || \{111\}_\gamma) to form a conceptual map of the orientation relationship (see figure 3.5). By manipulating the nets of figure 3.5, Young was able to describe
both the Kurdjumov-Sachs and Nishiyama-Wasserman orientation relationships
(see figure 3.5) [2].

Figure 3.5: Young’s description of the orientation relationship between austenite and ferrite. (111) austenite (the full lines in the figure) is assumed to be parallel to (110) ferrite (the dashed lines). It is also assumed that $[1\bar{1}1]_\alpha || [101]_\gamma$, i.e. this figure illustrates the Kurdjumov-Sachs O.R. However, if the (110) ferrite plane is rotated by $5.26^\circ$ in a counterclockwise direction, with respect to the $[1\bar{1}1]$ austenite, the N-W O.R. results. Adopted from ref [2].

In his 1926 paper, Young did not quote the orientation relationship as we would today. However, his schematic drawings of the relationship between trace
directions on the parallel \{111\}_α \parallel \{110\}_γ interface clearly demonstrate approximations to the Kurdjumov-Sachs (K-S) and Nishiyama-Wasserman (N-W) orientation relationships (O.R.) In his 1939 paper, Young makes reference to the Kurdjumov-Sachs and Nishiyama papers, and shows that his experimentally determined O.R.s are indeed approximations to the K-S and N-W orientations.

Young argues that the true orientation relationship lies somewhere between both N-W and K-S O.R., although he feels the K-S orientation relationship is “unnecessarily complicated and unsound theoretically” [2]. Modern studies of the ferrite – austenite O.R.s come to similar conclusions, i.e. the orientation relationship lies close to the K-S and N-W O.R.s.

In order to interpret the findings of Young and others, it is instructive to examine the relationship between the Kurdjumov-Sachs (K-S) orientation relationship (OR) and the Nishiyama-Wasserman (N-W) OR. Figure 3.5 shows the relationship between various FCC and BCC directions for a parallel (111)_γ \parallel (110)_α plane, whilst figures 3.6 (a) and (b) are stereographic projections of the body-centered cubic (BCC) and face-centered cubic (FCC) phases, respectively.
Figure 3.6: (a) Stereographic projection of the BCC ferrite phase centered on (110). (b) Stereographic projection of the FCC austenite phase centered on (111). Notice if images are overlaid $[111]_\alpha \parallel [\bar{1}1\bar{0}]_\gamma$ Created using SingleCrystal.
The Kurdjumov-Sachs (K-S) orientation relationship (Figures 3.5 and 3.6) defines a relationship between FCC and BCC crystals and can be quoted as:

\[
\begin{align*}
\text{1.} & \quad (111)_{\gamma} \parallel (110)_{\alpha} \\
\text{2.} & \quad [\bar{1}01]_{\gamma} \parallel [1\bar{1}1]_{\alpha}
\end{align*}
\] (1)

If the FCC crystal is rotated about the common \((111)_{\gamma} \parallel (110)_{\alpha}\) by 5.25 degrees, conceptualized by overlaying the two images in figure 3.6, in a counter-clockwise fashion, the \([\bar{1}10]\) direction of the FCC phase is brought into coincidence with the \([001]\) BCC direction. We have now generated the Nishiyama-Wasserman (N-W) orientation relationship, which may be written as:

\[
\begin{align*}
\text{1.} & \quad (111)_{\gamma} \parallel (110)_{\alpha} \\
\text{2.} & \quad [\bar{1}10]_{\gamma} \parallel [001]_{\alpha}
\end{align*}
\] (2)

If the FCC crystal is then rotated by a further 5.25 degrees, in a counter-clockwise direction, about the common \((111)_{\gamma} \parallel (110)_{\alpha}\), the \([01\bar{1}]_{\gamma}\) direction is brought into coincidence with the \([\bar{1}11]_{\alpha}\) direction, thus generating a second K-S orientation relationship, written as:

\[
\begin{align*}
\text{1.} & \quad (111)_{\gamma} \parallel (110)_{\alpha} \\
\text{2.} & \quad [01\bar{1}]_{\gamma} \parallel [\bar{1}11]_{\alpha}
\end{align*}
\] (3)

Hence, the variant of the N-W orientation quoted in (2) can be seen to be equiangularly displaced with respect to the two variants of the K-S orientation relationship. If we define a rotation angle \(\theta\), about the common \(\[111\]_{\gamma} \parallel [110]_{\alpha}\) axis such that \(\theta = 0\) corresponds to the N-W orientation relationship, then values of \(\theta = \pm 5.25\) degrees corresponds to the two neighboring K-S orientation.
variants. As seen in figure 3.3, the measured values for $\theta$ range between 0 and 8°, i.e., they encompass both the K-S and N-W O.R.s.

In Young’s study of the Canyon Diablo meteorite, about twenty ferrite precipitates were examined; fifteen of these particles exhibited a plate-like morphology and were characterized by $(111)_\gamma \parallel (110)_\alpha$. However, for six of the ferrite crystals an irregular morphology was determined and an orientation relationship which was far removed from either the K-S or N-W O.R.s was determined. Furthermore, many of these irregularly shaped ferrite precipitates were associated with schreibersite (an iron-nickel phosphide): it would appear that ferrite which nucleates on this particular inclusion does not develop a rational orientation relationship with respect to the austenite into which it is growing. This observation is of huge import; conventional wisdom would suggest that the O.R. that would develop between parent and product phase is independent of the nucleation site. However, Young’s data on the Canyon Diablo meteorite shows that this is not the case. Young was also able to show that in the Carlton meteorite, “…a strong maximum…not belonging to the Widmanstätten type of orientation…” was observed in addition to maxima characteristic of the K-S and N-W O.R.s [1, 2]. Again, Young associated the “rogue” reflections with precipitation of ferrite on schreibersite.
3.3 WIDMANSTÄTTEN FERRITE CRYSTALLOGRAPHY IN LOW ALLOY STEELS. THE KING AND BELL PAPERS.

Figure 3.7: Schematic drawing of the serial-sectioning method employed by King and Bell. Figure shows (schematic) Widmanstätten ferrite plates, shown in grey, within the austenite matrix. Each section was cut orthogonally from the specimen’s primary surface and imaged, creating a three-dimensional map, layer by layer. Black area in image serves only to give three-dimensionality to the schematic.

In the mid-1970s, King and Bell wrote a series of three manuscripts describing the morphology of proeutectoid ferrite and its orientation relationship with the austenite matrix in a low carbon steel [4-6]. King and Bell used Kossel x-ray diffraction to obtain patterns for the ferrite plates, which were later employed to find the four Widmanstätten ferritic habit planes and subsequently the orientation of the original austenite. The authors prepared samples by vacuum melting high-purity Fe-C alloys and homogenizing at approximately 1100 °C for various times. After this initial heat treatment, the authors isothermally held the
samples at approximately 730 °C (above the eutectoid temperature) for 20 minutes, and subsequently quenched [4, 5]. Using a serial sectioning method, King and Bell were able to produce a near three-dimensional image of ferrite plates within the sample. A schematic drawing of the serial sectioning technique is given in figure 3.7. Examination of the orthogonal surface slices allowed them to conclude that the Widmanstätten ferrite does, indeed, form close to the \{111\} planes of the austenite [4], i.e. King and Bell’s data are fully consistent with the results of Young [1, 2].

Comparisons of the orientation relationships between the ferrite plates and the austenite matrix led King and Bell to the conclusion that there is a “real spread of allowable orientation relationships” for Widmanstätten ferrite between Kurdjumov-Sachs (K-S) and Nishiyama-Wasserman (N-W) [4]. In this analysis 49 precipitates were studied and categorized by the deviation of the orientation relationship from the N-W relationship; the deviation being quantified by the parameters $\theta$, and $\phi$ (figure 3.3). King and Bell developed these comparisons by analyzing only austenite grains which included at least two of the forms of the ferrite \{111\} habit plane, which thus permitted the austenite orientation to be identified. All 49 precipitates corresponded to orientation relationships near the K-S and N-W relationships and furthermore had an average angle, $\theta$, of 3.3° from the N-W relationship [4]. Considering that the K-S relationship is merely a 5.25° rotation from the N-W relation, the precipitates had a closer association to the K-S relationship. Figure 3.8 plots the deviation of the orientation relationships from the N-W orientation relationship.
Figure 3.8: Distribution of ferrite-austenite orientation relationships as a function of the angle, $\theta$, between the [011]$_\gamma$ and [001]$_\alpha$ directions. Angles of 0 and 5.25 represent the N-W and K-S orientation relationships, respectfully. Adapted from King and Bell [4].

In the discussion of their methods, King and Bell describe the Widmanstätten proeutectoid formation as a purely diffusion controlled process. However, King and Bell also note that it has been proposed that ferrite forms via shear, as advanced by e.g., Clark and Wayman [4, 5]. This theory is later expanded by Goldstein in subsequent manuscripts.

In King and Bell’s second manuscript, they found that ferrite nucleated at grain boundaries such that there was an orientation relationship with respect to at least one of the abutting grains. Furthermore, the authors found that Widmanstätten ferrite could grow into matrix grains with which it shared an orientation relationship; however, ferrite may also grow into grains in which there
was no orientation relationship to the austenite matrix. This finding is in agreement with the work of Aaronson, referenced by King and Bell, who suggested that ferrite allotriomorphs, which formed at grain boundaries, have an O.R. with respect to one of the abutting grains, but could grow into that grain with which it did not bear an O.R.

In the third manuscript by King and Bell, the authors again analyzed the same Fe-C alloy by serial-sectioning in an attempt to understand the deviations associated with habit planes of ferrite in an austenite matrix. King and Bell found precipitates within five degrees of a \{111\} orientation. Using 22 Kossel patterns, King and Bell again found that the orientation relationship between ferrite and austenite encompassed that of the K-S and N-W orientation relationships.

Throughout the three manuscripts, King and Bell referred to the occurrence of sub-grain boundaries in, and polygonization within Widmanstätten ferrite as an explanation for the observation that slightly different orientations, within nominally single crystals of Widmanstätten ferrite, were frequently observed. A schematic drawing of sub-grains within Widmanstätten ferrite is illustrated in chapter 2, figure 2.13.

King and Bell found that adjacent sub-grains exhibited similar yet distinguishable Kossel patterns. It was initially thought that these sub-grains developed from a single, highly dislocated grain, which ultimately polygonized (as seen in figure 3.9). Polygonization occurs during annealing when “dislocations align themselves into walls to form small-angle or sub-grain boundaries” [7].
However, it was later suggested that sympathetic nucleation might serve as the true mechanism for the development of the sub-grain structure; King and Bell noted that a high density of dislocations would have to be present in a growing ferrite for a polygonization process to yield misorientations of one degree or more.

The concept of sympathetic nucleation becomes crucial in a series of later papers which deal with the development of Widmanstätten ferrite from grain boundary allotriomorphs. These latter studies are discussed in section 3.4.2.

3.4 THE CRYSTALLOGRAPHY OF GRAIN BOUNDARY ALLOTRIOMORPHS IN STEELS

3.4.1 Data From A Silicon Steel

In 1991, Babu and Bhadeshia produced a manuscript describing allotriomorphic ferrite’s orientation relationship to the austenite grain into which
it grew. The purpose of their work was to determine the likelihood for
Widmanstätten ferrite formation from an allotriomorphic host. Babu and
Bhadeshia showed that the orientation relationship between allotriomorphic ferrite
and its host austenite grain was, for the most part, random [8]. This conclusion
was reached by measuring the angle, $\varphi$, between the $\{111\}_\gamma$ and $\{011\}_\alpha$ planes,
and $\theta$, the angle between the $<10\overline{1}>_\gamma$ and $<11\overline{1}>_\alpha$. In Babu and Bhadeshia’s
experiments, the angles of both $\theta$ and $\varphi$ frequently exceeded 20° [8], it was thus
concluded that the allotriomorphic ferrite was unlikely to nucleate Widmanstätten
ferrite.

Babu and Bhadeshia also measured the orientation relationships between bainite
and austenite, finding that bainite was invariably related to the parent austenite. A
comparison of the bainite and allotriomorphic orientation relationships to
austenite can be seen in figure 3.10, note the proximity of bainite to N-W or K-S
when contrasted to its allotriomorphic counterpart.
3.4.2 Sympathetic Nucleation And The Development Of Widmanstätten Ferrite

“Sympathetic nucleation is defined as the nucleation of a precipitate crystal at an interphase boundary of a crystal of the same phase when these crystals differ in composition from their matrix phase throughout the transformation process.” [9]

In 2004, Phelan and Dippenaar published two papers which focused on intergranular Widmanstätten ferrite nucleation and its mechanism of formation [10]. The authors describe the ongoing debate as to whether Widmanstätten ferrite nucleates via an instability mechanism at the interface or via sympathetic nucleation. According to the authors, Mullins and Sekerka, developed a model to simulate the Widmanstätten ferrite formation via interfacial instability, which later was tested by Townsend and Kirkaldy [10]. Townsend and Kirkaldy advanced the idea that allotriomorphs may provide the instabilities for initial Widmanstätten ferrite nucleation. However, Phelan and Dippenaar rather convincingly showed that the interfacial instability mechanism is not operative.

The authors then tested the theory of sympathetic nucleation of Widmanstätten ferrite using orientation imaging in the scanning electron microscope (OIM). The authors prepared samples from low-carbon alloys by heating them to 1450 °C for 10 minutes. They then cooled the samples to 1350 °C, held for 10 minutes, and finally cooled to 700 °C at a rate of 100 °C/min. Lastly, they held the samples isothermally at 700 °C until all transformations were complete [10]. It was found through electron backscatter diffraction (EBSD)
analysis that there was a misorientation between the intergranular Widmanstätten ferrite and the pre-existing allotriomorphic ferrite. Considering that there is near orientational uniformity (< 1 degree change) within the Widmanstätten ferrite and within the allotriomorph, but a six degree difference between the two, the authors state that this is inconsistent with an instability mechanism. An instability mechanism, according to Phelan and Dippenaar, requires that the allotriomorphic ferrite and Widmanstätten ferrite be of single orientation.

In a subsequent manuscript, Phelan, Dippenaar and Stanford [11], presented in situ observations of Widmanstätten ferrite formation via high temperature laser scanning confocal microscopy. Phelan et al [11] used this in situ analysis to contrast the growth morphologies of ferrite allotriomorphs and Widmanstätten ferrite. The authors also used OIM to examine the orientation difference between allotriomorphic ferrite and Widmanstätten ferrite.

Phelan et al observed that Widmanstätten ferrite plates grew at increasingly rapid rates as they lengthened from the allotriomorphic host. Phelan et al believed that these differing growth rates were results of plate orientations which were evolving dynamically towards the K-S/N-W orientation relationships via multiple nucleation events, which eventually developed a fast growth orientation.

In an attempt to understand the orientational changes required to form Widmanstätten ferrite, Phelan et al first outlined their assumptions concerning both allotriomorphic ferrite and Widmanstätten ferrite. Their assumptions are as follows:
1. Widmanstätten ferrite’s fast growth orientation (final orientation) is associated with the Young-Kurdjumov-Sachs orientation relationship (see section 3.2).

2. Grain boundary allotriomorphs rarely exhibit an exact K-S/N-W orientation relationship with respect to abutting grains.

3. Sympathetic nucleation produces an orientation change, with an ideal allotriomorph having only 1-2° of misorientation between it and its Widmanstätten precipitate.

Phelan et al, however, most often found orientations between the fast growing Widmanstätten ferrite and ferrite allotriomorphs to be near 9°. The authors then postulate that the final ferrite orientation is produced incrementally through intermediate, or bridging orientations.

According to this 2005 manuscript, “…the observation of low angle boundaries between Widmanstätten plates and grain boundary allotriomorphs … has cemented the view that Widmanstätten plates form by sympathetic nucleation on pre-existing grains.” In general, it is believed that, sympathetic nucleation results in a low angle ferrite/ferrite grain boundary, which Phelan et al empirically describe through the Read-Shockley equation (4).


\[
\gamma_{\alpha/\alpha} = \frac{Gb\theta}{4\pi(1-v)} \left( \ln \frac{b}{b_0} - \ln \theta \right)
\]

(4)
where $\gamma_{\alpha/\gamma}$ is the ferrite grain boundary energy, $G$ is the shear modulus, $b$ is the burger’s vector, $\nu$ is the poisons ratio, $\theta$ is the misorientation, and $b_0$ is a constant equal to 0.75$b$, with the energy barrier to sympathetic nucleation ($\Delta G^*$) (5):

$$\Delta G^* = \frac{16\pi (\gamma_{\alpha/\gamma})^2 \gamma_{\alpha/\alpha}}{\Phi^2},$$

(5)

where $\gamma_{\alpha/\gamma}$ is the phase boundary energy and $\Phi$ is the sum of the volume free energy change, to produce (6):

$$\Delta G^* = K\theta \left( \ln \frac{b}{b_0} - \ln \theta \right),$$

(6)

where $K = \frac{4Gb(\gamma_{\alpha/\gamma}^2)}{(1-\nu)\Phi^2}$.

According to Phelan et al, this equation defines a maximum misorientation for sympathetic nucleation of about 15°. Figure 3.11 represents the energy barrier to nucleation as a function of the misorientation angle.
In 2005 Kral and Spanos published two manuscripts regarding a three-dimensional analysis of proeutectoid ferrite [12, 13]. Although King and Bell had employed serial sectioning to obtain three-dimensional information, the computing power for three-dimensional rendering was not yet available. However, Kral and Spanos had the ability for computer aided three-dimensional reconstructions, which revealed, sometimes subtle, sometimes significant differences between previous works and their manuscript regarding the morphology of proeutectoid ferrite. In their experiment, samples were created from high purity Fe – 0.12% C – 3.28% Ni alloys, which were homogenized for 3 days at 1250 °C. They were then austenitized at 1300 °C for 1500 seconds, and
lastly isothermally reacted at 650 °C for various times [12, 13]. The results from this experiment resulted in the morphologies illustrated in figure 3.12.

Figure 3.12: Dube Classification System compared to Kral and Spanos Classification System. a) Primary ferrite side plates, developed directly from austenite grain boundaries. b) Secondary ferrite side plates connected to grain-boundary allotriomorphic ferrite. c) Primary ferrite saw teeth developed directly from austenite grain boundaries. d) Secondary saw teeth connected to grain-boundary allotriomorph ferrite. e) Grain-boundary idiomorph/allotriomorphs, which lie on the grain boundary - shape approximately an ellipsoid. The images f) – j) are three-dimensional representations of a) – e), respectively. Adapted from [12, 13].
In the analysis of Kral and Spanos, the authors find that their primary ferrite are the shape of a triangular pyramid or spike, with a baseline in the plane of the grain boundary, as seen in figure 3.13 or figure 3.12 a) and f).

![Figure 3.13: The primary Widmanstätten ferrite spikes of Kral and Spanos. Recreated from [12].](image)

In agreement with Phelan and Dippenaar, Kral and Spanos described Widmanstätten ferrite structures that were not monolithic single crystals, but were made up of many smaller grains. Kral and Spanos noted the importance of this distinction and attributed secondary side plate formation to sympathetic nucleation. In their companion paper, the authors used orientation imaging to compare the allotriomorphic ferrite’s orientation with that of the Widmanstätten ferrite’s orientation. The authors constructed a misorientation map of ferrite side plates, and showed that, Widmanstätten ferrite forms with a misorientation with respect to the ferrite allotriomorph, which suggests sympathetic nucleation.
According to Kral and Spanos, there was nearly a six degree misorientation between the allotriomorphic ferrite and the Widmanstätten ferrite. The authors also showed that the ferrite slowly approached a common orientation; however, the data suggested repeated nucleation of small orientational changes. According to Kral and Spanos, “the ferrite branches are obviously not monolithic single crystals formed by a solid-state instability mechanism” [13]. According to the authors, it seemed likely that Widmanstätten ferrite forms via sympathetic nucleation from allotriomorphic sites.

3.5 AN EMERGING VIEWPOINT ON THE CRYSTALLOGRAPHY OF FCC/BCC SYSTEMS

In a series of seminal papers in the early part of the twentieth century, Young described the orientation relationships developed between intragranularly nucleated Widmanstätten ferrite and austenite [1, 2]. For the Widmanstätten ferrite that nucleated in the absence of a substrate, the Kurdjumov-Sachs (K-S) or the Nishiyma-Wasserman (N-W) orientation relationships (O.R.s) were documented, as was a near \{111\}_\gamma habit plane. A second grouping of ferrite precipitates, those which had nucleated on a substrate (i.e., schreibersite), exhibited neither a Widmanstätten morphology nor an N-W/K-S O.R.

More recently, in a wide-ranging paper on the precipitation of phosphides in a variety of medium-nickel meteorites, Clarke and Goldstein [14] showed that ferrite which was associated with schreibersite was not Widmanstätten in character, but adopted an allotriomorphic or swathing morphology. One may
safely conclude from the data of Young [1, 2] and Clarke and Goldstein [14], that the orientation relationship between inclusion nucleated ferrite and austenite is not within the K-S/N-W orientation region and that this ferrite can not develop directly into Widmanstätten ferrite. The question then remains; what does control the orientation of inclusion nucleated ferrite? We will return to this question later in this section.

In a series of papers in the 1970s, King and Bell [4-6] examined Widmanstätten precipitates in a steel; also describing a near K-S/N-W orientation and a \( \{111\} \gamma \) habit plane for the ferrite. King and Bell also showed that grain boundary nucleated (i.e. intergranular) ferrite was rationally related to at least one of the abutting austenite grains, also by the K-S/N-W O.R. The results of King and Bell were sufficiently compelling that Howell and Honeycombe [15] postulated that there were two processes that could influence/control the orientation variant(s) selected by a grain boundary precipitate:

(i) The Habit-Plane Hypothesis

(ii) A Three-Phase Crystallography

The habit plane hypothesis suggests that precipitates can lower the energy barrier to nucleation by minimizing the angle between a low energy facet plane and the local grain boundary plane. If this were to be the case for the formation of intergranular Widmanstätten ferrite, then it would be expected that the \( \{111\} \gamma \parallel \{110\} \alpha \) interface would be almost parallel to the local grain boundary plane orientation; in fact this is not observed.
The three-phase crystallography hypothesis suggests that the daughter phase, e.g., ferrite, would adopt an orientation which allowed it to develop low energy interfaces with respect to both abutting parent grains, e.g., austenite. The data of King and Bell [4-6] would tend to support this hypothesis.

However, in 1991, Babu and Bhadeshia [8] showed that in a silicon steel, the vast majority of grain boundary allotriomorphs were not related to the austenite grain into which they were growing by the K-S/N-W orientation (see figure 3.10a). Babu and Bhadeshia explained their data in terms of the following:

(i) A grain boundary allotriomorph of ferrite nucleated at an austenite grain boundary and with a rational orientation relationship with respect to one of the abutting austenite grains;

(ii) Rapid growth of the allotriomorph along the grain boundary and through triple junctions led to ferrite growth into austenite grains, which the ferrite was not in contact with during nucleation;

(iii) Therefore, the orientations observed relate to selective growth only, not nucleation.

Although, the above argument is feasible, it is also possible that the nuclei themselves developed with an orientation that was not governed by either the habit-plane hypothesis or three-phase crystallography.

The studies of Kral and Spanos [12, 13] and of Dippenaar and co-authors [10, 11] is relevant in this regard because these authors found that Widmanstätten ferrite could not develop directly from grain boundary allotriomorphic ferrite. Rather, separate nucleation events, involving multiple events of sympathetic
nucleation, led to the development of Widmanstätten ferrite in contact with the allotriomorphic ferrite. Unfortunately, neither Kral and Spanos \[12, 13\] nor Dippenaar and co-workers \[10, 11\] were able to reconstruct the orientation of the austenite into which the ferrite was growing, but their OIM data clearly shows that there is a significant orientation difference (~ 6°) between Widmanstätten ferrite side-plates and the allotriomorphic ferrite.

In summary, it would appear that, for nucleation of ferrite, in the absence of a catalyzing substrate (i.e., an inclusion or a grain boundary), the ferrite adopts the K-S/N-W O.R. with respect to the austenite. The ferrite may also develop as Widmanstätten ferrite with a \{111\}_\gamma || \{110\}_\alpha habit plane. However, when ferrite develops on a substrate, i.e., an inclusion or grain boundary, the orientation may not correspond to the K-S/N-W O.R., and the morphology is allotriomorphic rather than Widmanstätten. This allotriomorphic ferrite may develop into Widmanstätten ferrite by the process of sympathetic nucleation, if the orientation of the original allotriomorphic ferrite is close to that (perhaps within 6° or so) of K-S/N-W.

There appears to be several possibilities for what controls the orientation of substrate-nucleated ferrite. These are listed as follows:

(i) habit plane orientation
(ii) the orientation of the austenite matrix
(iii) the orientation of the substrate (e.g. schreibersite)
(iv) some form of three-phase crystallography
We may discount possibility (i) since intergranular Widmanstätten ferrite only forms with its habit plane at a high angle to the average grain boundary plane [10].

Possibility (ii) would yield the conventional orientation (K-S/N-W). That this may occur is implicit in the many studies on acicular ferrite in steel welds [8], where it has been shown that Widmanstätten ferrite forms on weld-metal inclusions. One may assume that the inclusion nucleated ferrite has the same orientation as e.g., the bainite in Babu and Bhadeshia’s study (see figure 3.10b).

Possibility (iii) is intriguing, if the substrate governs the orientation relationship of the nucleated phase, then the orientation relationship between the nucleated phase (ferrite) and the parent phase (austenite) may not be that which is normally observed. As an example, consider the formation of the carbide NbC in austenite and the subsequent formation of ferrite on the NbC/γ interface. It is known, that the NbC is related to the γ by the cube-cube O.R., as shown in (7):

\[
\{100\}_{\text{NbC}} \parallel \{100\}_\gamma \\
<100>_{\text{NbC}} \parallel <100>_{\gamma}
\] (7)

If the orientation of the ferrite is controlled by the orientation of the carbide, then the α and NbC will be related by the Baker-Nutting (B-N) O.R., as shown in (8):

\[
\{100\}_{\text{NbC}} \parallel \{100\}_\alpha \\
<100>_{\text{NbC}} \parallel <110>_{\alpha}
\] (8)

Hence, the α and the γ would also be related to each other by the B-N O.R. (9),

\[
\{100\}_\alpha \parallel \{100\}_\gamma \\
<110>_{\alpha} \parallel <100>_{\gamma}
\] (9)
which is different from the K-S/N-W O.R. Is it reasonable to expect ferrite to nucleate with an orientation relationship with respect to the substrate, rather than the parent? The application of classical nucleation theory can, at least partially, answer this question.

Figure 3.14: Illustrations of ferrite nucleation. a) represents homogeneous nucleation in an austenite matrix, b) represents low energy faceted homogeneous ferrite nucleation in austenite, c) represents heterogeneous nucleation on an inclusion d) represents the replacement of high energy interfaces of austenite - inclusion with that of lower energy interfaces of ferrite - inclusion, and e) represents the replacement of low energy interfaces of austenite - inclusion with that of high energy ferrite - inclusion interfaces, with the inclusion of faceting.
Figure 3.14a shows the morphology of a homogeneously nucleated, unfaceted sphere of ferrite in the austenite matrix. The energy barrier to nucleation ($\Delta G^*_{\text{hu}}$) is given as:

$$\Delta G^*_{\text{hu}} = \frac{16\pi\gamma^3}{3\Delta G^2_{\gamma}}$$

(10)

If we assume that the ferrite nucleus ($\alpha$) is truncated by low-energy facet that are parallel to $\{111\}_{\gamma} \parallel \{110\}_\alpha$ (figure 3.14b) then the nucleus morphology of figure 3.14b results and the energy barrier to nucleation is:

$$\Delta G^* = \Delta G^*_{\text{hu}} \cdot (1 - 2f(\theta))$$

(11)

If we now consider nucleation of inclusion (I), we will first assume that the inclusion has nucleated in austenite ($\gamma$) and with a rational orientation relationship (O.R.). Hence the inclusion / austenite interfaces ($\gamma_{I\gamma}$) will be relatively low energy. Let us now assume that ferrite nucleates on the inclusion / austenite interface, producing a ferrite / inclusion interface of low energy ($\gamma_{I\alpha}$). If we further assume that

$$\gamma_{I\gamma} \cong \gamma_{I\alpha}$$

(12)

then the dihedral angle will be $\cong 90^\circ$ (figure 3.14c) and the energy barrier to nucleation will be:

$$\Delta G^* = \frac{\Delta G^*_{\text{hu}}}{2}.$$  

(13)

However, it is likely that, at a particular orientation of the inclusion / austenite interface, a relatively high energy austenite / inclusion interface can be replaced

---

1 This is a reasonable assumption because Clarke and Goldstein showed that massive schreibersite formed at approximately 800 °C.
by a lower energy ferrite / inclusion interface. In this instance, the dihedral angle, \( \phi \), will be less than 90° (figure d) and

\[
\Delta G^* = \Delta G_{hu} * f(\phi)
\]

(14)

If we now turn to the conventional situation where the ferrite nucleates on the substrate, but with an O.R. with respect to the parent phase, than a relatively low energy inclusion / austenite interface will be replaced by a higher energy ferrite / inclusion interface and the dihedral angle (\( \phi \)) will be greater than 90°. In the absence of faceting, the energy barrier to nucleation is

\[
\Delta G^* = \Delta G_{hu} * (1 - f(180 - \phi))
\]

(15)

And in the presence of faceting (figure 3.14e)

\[
\Delta G^* = \Delta G_{hu} * (1 - \{f(180 - \phi) + f(\theta)\})
\]

(16)

Depending on the relative values of the interfacial energies, it is feasible that nucleation on a substrate will favor the development of a ferrite / substrate O.R. rather than a ferrite / austenite O.R.

### 3.6 Crystallography of Widmanstätten Ferrite

In the present investigation, the misorientation between swathing ferrite and Widmanstätten ferrite, in the Brenham meteorite was analyzed, using electron backscatter diffraction (EBSD) coupled with computer-controlled orientation imaging microscopy (OIM).

In figure 3.15 and 3.16, OIM analyses of Widmanstätten ferrite and the associated swathing ferrite are shown. The misorientations between these two
species in each figure are shown in Figures 3.15 b) and c) and 3.16 b) and c), respectfully. In all cases, the misorientation between the ferrite allotriomorphs and Widmanstätten plates were in excess of 15°. Therefore, it can be concluded that sympathetic nucleation cannot serve as a mechanism for the nucleation of Widmanstätten ferrite.

Misorientations were also determined between sub-grains within the Widmanstätten ferrite plates. According to figure 3.17 b) and c), it is possible, that once formed, Widmanstätten ferrite can subsequently form sympathetically. The small angle of misorientation within the plates suggests that there was a low energy barrier to nucleation. However, it is also possible that the sub-boundaries seen in, e.g. figure 3.17 a), were formed by polygonization.

Reference to Figures 3.15, 3.16, and 3.17 show no evidence for the bridging nucleation of Phelan et al., i.e., there is a sharp, singular discontinuity in orientation between the swathing ferrite and the Widmanstätten ferrite. Hence, we can conclude that the swathing ferrite does not act as nucleation substrate for Widmanstätten ferrite.
Figure 3.15: OIM images of Widmanstätten ferrite association with swathing ferrite. Lines on image represent misorientation scans. The misorientation between swathing ferrite and adjacent Widmanstätten plates is in excess of 15°, the maximum misorientation for sympathetic nucleation as a nucleation mechanism according to Phelan and Dippenaar. The letter S in the drawing represents swathing ferrite and W represents Widmanstätten ferrite.
Figure 3.16: OIM images of Widmanstätten ferrite is association with swathing ferrite. Lines on image represent misorientation scans. The misorientation between swathing ferrite and adjacent Widmanstätten plates is in excess of 15°, the maximum allowable misorientation for sympathetic nucleation as a nucleation mechanism. The letter S in the drawing represents swathing ferrite and W represents Widmanstätten ferrite.
Figure 3.17: a) Misorientation map across Widmanstätten ferrite sub-grains. Notice the misorientation is below 3° in both cases b) and c). Therefore sympathetic nucleation was a viable option as its nucleation mechanism.

3.7 SUMMARY

This chapter has reviewed the crystallography of the ferrite reaction in iron-nickel meteorites. The work of Young in the 1920s and 1930s showed that Widmanstätten ferrite forms with an orientation relationship (O.R.) which is close to the Kurdjumov-Sachs (K-S) and Nishiyama-Wasserman (N-W) O.R.s. Conversely, the swathing ferrite does not adopt a near K-S or N-W O.R. Although, Young’s studies were published well over 50 years ago, their
significance seems to have been overlooked. The results of our investigation, together with the results of others, strongly suggest that swathing ferrite forms on inclusions, whereas Widmanstätten ferrite does not. It has been postulated that it is the orientation of the inclusion that influences the orientation of the swathing ferrite, rather than the orientation of the single crystal austenite. Furthermore, our OIM studies indicate that the misorientation between swathing ferrite and Widmanstätten ferrite is so large that it prevents the sympathetic nucleation of the latter on the former.
References:

CHAPTER 4: CONCLUSIONS AND FUTURE WORK

4.1 INTRODUCTION

This chapter serves to collate the disparate pieces of information presented in Chapters 2 and 3 into a coherent whole. We will aim to show that Widmanstätten ferrite forms over a wide temperature range and that nucleation may occur in a series of bursts. However, the major conclusion is that nucleation of Widmanstätten ferrite does not occur at a single temperature, or even over a small temperature interval. We shall also argue strongly that the term Widmanstätten ferrite be used to replace such terms as “acicular” or “spindle-like” ferrite and that the terms comb plessite and net plessite be dropped in favor of (degenerate) Widmanstätten ferrite.

We shall also argue, both from our own data and from a detailed literature review, that the precipitation of phosphides is not necessary for the formation of Widmanstätten ferrite. Rather Widmanstätten ferrite forms in regions that are remote from massive schreibersite (phosphide inclusion) and indeed from other inclusions. Massive schreibersite is found to nucleate ferrite, but this ferrite is of the allotriomorphic (swathing) variety. It is suggested that swathing ferrite does not form with either an approximate Kurdjumov-Sachs (K-S) or Nishiyama-Wasserman (N-W) orientation relationship. It is also argued that swathing ferrite does not act as a nucleation substrate for Widmanstätten ferrite.
## 4.2 PHASES AND MICROCONSTITUENTS

Table 4.1: Types of Plessite.

<table>
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<tr>
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<tbody>
<tr>
<td>Type I (Fine Widmanstätten ferrite in austenite)</td>
<td>Acicular Plessite</td>
<td>“Immature” Widmanstätten ferrite. Tertiary Widmanstätten ferrite.</td>
<td>Cape York, Henbury</td>
</tr>
<tr>
<td>Type II (Virgin martensite)</td>
<td>Black Plessite</td>
<td>Plate martensite for nickel contents in excess of 25-30%. Lath martensite for lower nickel contents.</td>
<td>All</td>
</tr>
<tr>
<td>Type III (Tempered martensite)</td>
<td>Cellular Plessite</td>
<td>Tempered lath martensite. (The plate martensite probably forms at too low a temperature to significantly temper.)</td>
<td>All</td>
</tr>
<tr>
<td>Net Plessite/Comb Plessite</td>
<td>Secondary Widmanstätten ferrite. Degenerate Widmanstätten ferrite.</td>
<td>Cape York, Henbury, Brenham</td>
<td></td>
</tr>
<tr>
<td>Pearlitic Plessite</td>
<td>Predominantly lamellar plessite, that forms via a monotectoid reaction (from austenite), or a discontinuous reaction (from martensite).</td>
<td>Canyon Diablo</td>
<td></td>
</tr>
<tr>
<td>Spheroidized Plessite</td>
<td>Non-lamellar plessite. May form by a discontinuous coarsening reaction, i.e., spheroidized plessite could replace lamellar plessite.</td>
<td>Canyon Diablo</td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1 lists the types of plessite that have been described by Massalski et al [1] and by Buchwald [2], together with some of our own comments. Our
results would suggest that the two major microconstituents in plessite regions are Widmanstätten ferrite (both secondary and tertiary) and martensite. We would also suggest that the terminology “acicular ferrite” and “comb / net” plessite be dropped in favor of the terms secondary / tertiary Widmanstätten ferrite. The discussion with respect to figure 2.10 establishes the plate-like nature of what is termed acicular or spindle-like ferrite, whereas the microprobe traces which are associated with the “acicular ferrite” of figure 2.25 prove unambiguously that these ferritic units are indeed growing under full diffusion control, i.e., they are plates of Widmanstätten ferrite and not martensite. We have also argued that the comb / net microstructures of e.g., figures 2.14 a and b derive from closely spaced Widmanstätten ferrite plates which are modified by a combination of polygonization and coarsening to yield a “degenerate Widmanstätten structure;” mechanisms for the coarsening of entrapped pools of austenite have been presented with respect to figures 2.15 – 2.17.

A simple model for the development of the Widmanstätten morphology was described with respect to figure 2.11 and it is argued that acicular / spindle-like ferrite is better described as having a double spherical cap morphology; a shape that arises due to the rapid lengthening kinetics of the Widmanstätten ferrite and the relatively slow thickening kinetics (see figure 2.11).

---

1 For the present discussion, we will ignore the high-nickel retained austenite and its decomposition products in the rim-region. We shall also ignore the pearlitic plessite, which is found in e.g., the Canyon Diablo meteorite.
4.3 THE NUCLEATION TEMPERATURE FOR WIDMANSTÄTTEN FERRITE

Yang and Goldstein [3] have argued for a single nucleation temperature, i.e., one that corresponds to either the crossing of the $(\alpha + \gamma + \text{Ph})$ boundary or the $M_s$ temperature. Our results strongly suggest that Widmanstätten ferrite nucleation occurs over a wide temperature range. The size distributions that were presented in figures 2.20 and 2.22 show that the ferritic band widths vary by over three orders of magnitude; such a size range can hardly be explained in terms of a single nucleation burst. The result presented in figures 2.20 and 2.22 can not be explained by sectioning effects related to the orientation of the surface, nor by sectioning of Widmanstätten plates close to their periphery. For example, the sample surface for the data that are shown in figure 2.20 is close to $(001)$ and the only effect of orientation is to shift the entire distribution to smaller bandwidths by a factor of $\cos(54^\circ 44')$ or 0.57. Sectioning of a Widmanstätten plate close to its periphery will yield smaller apparent bandwidths; however, the effect in the overall size distribution is small.

Our microprobe data (see figures 2.25 et seq and table 2.2) may also be interpreted in terms of a range of nucleation temperatures. For example, the tertiary plates of figure 2.24 nucleated in an austenite matrix that was significantly enriched in nickel prior to their formation (e.g., see figure 2.25) and the limited extent of the diffusion profiles that are associated with secondary / tertiary Widmanstätten ferrite, as compared with the wide diffusion profiles that are associated with the primary Widmanstätten ferrite, also argues for large differences in the temperature of nucleation.
One of the more intriguing questions related to the size distribution of figures 2.20 and 2.22 is that of the nature of the distribution; are they truly bimodal / trimodal or do we have insufficient data to make such a determination? The first peak in the distribution, which is centered around 1 mm for the Cape York and Henbury meteorite, is that which all previous studies have concentrated on. The Widmanstätten plates which constitute this population dominate the visual appearance of a meteorite and the bandwidths that are quoted by e.g., Buchwald [2], refer to this grouping only. This primary Widmanstätten pattern partitions the austenite into numerous smaller units, which will later be given the collective term “plessite.” It is within these plessitic areas that the secondary and tertiary Widmanstätten ferrite forms. Certain pools of plessite are comprised predominantly of secondary Widmanstätten ferrite plates (e.g., figures 2.4, 2.8, and 2.14), which are separated by thin films of retained austenite (e.g., figure 2.4) or by discrete islands of austenite (figure 2.14). These secondary Widmanstätten plates constitute the second distribution, which is centered around 50 – 100 microns (e.g., figure 2.22). The third component of the size distribution, the tertiary Widmanstätten ferrite is typically the finest, with a bandwidth of 20 microns or less, and is found as more isolated plates in either black plessite (figures 2.10 and 2.21) or in films of retained austenite that lie between primary Widmanstätten ferrite plates (figure 2.24).

If we can conclude that these three size grouping are indeed distinct, then it would imply that during cooling, nucleation of Widmanstätten ferrite occurred in a series of bursts, and not continuously as a function of decreasing temperature.
In order to confirm that the size distribution is indeed multimodal, several sections of e.g., the Cape York meteorite and from different sources would need to be examined. However, Buchwald [2] does point out that each individual meteorite slice is broadly representative of the meteoritic structure as a whole. However, it should be noted that the bandwidth quoted by Buchwald for the Brenham meteorite is 0.8 mm [2]; yet we find a maximum bandwidth of less than 0.2 mm (see figure 2.32). Indeed, it is likely that our sample of the Brenham meteorite contains no primary Widmanstätten ferrite; i.e., the plate-like ferrite in figures 2.32 and 2.33 is all located with a wide plessite field and should be considered as secondary Widmanstätten ferrite.

4.4 THE LEDGE MECHANISM OF WIDMANSTÄTTERN FERRITE PLATE GROWTH

In developing a simple model for the development of the Widmanstätten plate morphology (figure 2.11) we invoked the ledge mechanism of precipitate growth. The ledge mechanism was first formulated by Aaronson in 1962 [4], and specifically for the thickening of Widmanstätten ferrite in steels. The ledge mechanism predicts a slow growth rate, one which is controlled by the nucleation of ledges and their subsequent lateral growth across the broad faces of the intrinsically immobile interface; it is also unlikely that an interface that is growing via the ledge mechanism will grow at a rate which is under full diffusion control. However, all of the studies which model the thickening rate of Widmanstätten ferrite (e.g., see ref [4]) assume full diffusion control and indeed the observation
of the M-profile in countless microprobe traces (e.g., see figure 2.7) would surely argue for full diffusion control. So does Widmanstätten ferrite in meteorites thicken via the ledge mechanism? And if not, is the mechanism for the morphological development of Widmanstätten ferrite, outlined with respect to figure 2.11, in error?

To answer the first question, we have found no evidence for ledges on the austenite / ferrite interfaces, indeed we have found little evidence for the intrinsic immobility of the (approximate) \( \{111\}_\gamma \parallel \{110\}_\alpha \) interface; it is rare to find a \( \gamma/\alpha \) interface that is planar over much of its length. The lack of evidence for ledges does not invalidate our argument concerning precipitate morphology; we simply need to invoke a thickening rate which is under full diffusion control (relatively slow) and a lengthening rate which is far faster than would be permitted by full diffusion control (reference to figures 2.27 and 2.28 demonstrates the very narrow diffusion profile that are developed by plate lengthening).

4.5 POLYGONIZATION IN WIDMANSTÄTTEN FERRITE

Reference to figures 2.4, 2.8, 2.13, and 2.28 show that many of the Widmanstätten ferrite plates contain sub-boundaries. These sub-boundaries could arise due to polygonization of deformation, induced by either the transformation strains or from extra-terrestrial collisions, or could result from sympathetic nucleation of one ferrite sub-unit on another. Sympathetic nucleation is dealt with in detail in Chapter 3, but our results suggest that polygonization is the more
likely mechanism through which these boundaries are formed. Transformation strains are generated and the observation of deformation twins (e.g., see figure 2.1) is strong evidence for shock deformation.

Conversely, sympathetic nucleation is frequently seen as the process that converts allotriomorphic ferrite to Widmanstätten ferrite (Chapter 3); such a change in morphology and growth mode is not required in meteorites where all evidence would suggest that the Widmanstätten morphology is maintained from the initial nucleation stage to the final growth process. Our OIM data (see figures 3.16 and 3.17) show that the internal boundaries in primary Widmanstätten plates are indeed low angle with a typical misorientation of $3^\circ$ and less.

4.6 THE EFFECT OF PHOSPHIDES ON THE FORMATION OF WIDMANSTÄTTEN FERRITE

A review of the literature suggests that phosphides are present predominantly as massive schreibersite, which may be in the millimeter size range or as rhabdites in the micron size range\(^2\) (see figures 2.29 and 2.30). The massive schreibersite form in the austenite whereas the rhabdites form in the ferrite. There is no evidence, either from the pre-existing literature, or from the present study that the phosphides act as nucleation sites for Widmanstätten ferrite in metallic meteorites. Even if the massive schreibersite were to act as heterogeneous nucleation sites for Widmanstätten ferrite, their very low number density can not be reconciled with the observed distribution of Widmanstätten ferrite. Moreover,

\(^2\) There are also microrhabdites and grain boundary schreibersite, but were only observed infrequently in the present study.
both schreibersite and other inclusions act to nucleate swathing ferrite and not
Widmanstätten ferrite (e.g., see figures 2.31, 2.32, and 2.33). The results of
Chapter 3 also suggest strongly hat swathing ferrite does not act as a nucleation
substrate for Widmanstätten ferrite; the misorientation between the two ferrite
products exceeds 15°.

4.7 SUGGESTION FOR FUTURE WORK

The totality of evidence supports the conclusion that acicular or spindle-like ferrite is indeed Widmanstätten ferrite and adopts a plate-like morphology.
For example, the identical spatial orientation of the primary and secondary
Widmanstätten ferrite (e.g., see figures 2.1, 2.4, 2.5, and 2.31) and the virtually
complete absence of equiaxed images of secondary Widmanstätten ferrite in our
two-dimensional cross-sections is conclusive evidence that the only difference
between what we term secondary Widmanstätten ferrite and primary
Widmanstätten ferrite is one of size. Moreover, their morphologies and spatial
orientations are virtually identical (some subtle differences are observed, e.g., see
figure 2.11), but these differences do not alter the conclusion that secondary and
tertiary Widmanstätten ferrite are plate-like. However, it is suggested that the
details of the shape of the Widmanstätten ferrite be analyzed using either a serial
sectioning technique or two-surface trace analysis; this will permit the
reconstruction of the detailed shape of the secondary and tertiary Widmanstätten
ferrite plates.
The results of the OIM experiments must be considered as preliminary. Further misorientation scans between swathing and Widmanstätten ferrite need to be performed. The Canyon Diablo meteorite merits further investigation to determine the relationship between massive schreibersite and swathing ferrite. The microprobe data of figures 2.7, 2.25, 2.26, 2.27, and 2.28 provide unambiguous evidence for a range in nucleation temperatures. However, we have not analyzed the diffusion profiles associated with tertiary Widmanstätten ferrite and this needs to be done. In addition, we need more data in the diffusion profiles that are associated with the lengthening of secondary / tertiary Widmanstätten ferrite; at present, our data are compromised by the overlap of diffusion fields. Finally, we need to analyze other sections of e.g., the Cape York meteorite in order to differentiate between the possibility of nucleation bursts as opposed to continuous nucleation of Widmanstätten ferrite over a broad temperature range.
References:


APPENDIX: EXPERIMENTAL METHODS

A.1 SAMPLE PREPARATION

The meteorites, which were analyzed in this thesis, were the Cape York, Canyon Diablo, Henbury, and Brenham meteorites. The meteorite samples were prepared and studied through standard metallographic procedures, where each sample was cut from a bulk meteorite specimen. The sample was then ground flat at 180 grit using a LECO DS-20 belt sander and mounted in 1.25 inch cylindrical Bakelite mounts using a ALLIED TECHPRESS 2 mounting press. After the sample was successfully mounted, they were polished. Using an ALLIED METAPREP 4 auto polisher, each sample was sanded successively on silicon carbide sandpaper of grits 240, 320, 600, and 800 until a smooth finish was obtained. Each sample was then polished using 1 micron alpha alumina power mixed with distilled water, followed by 0.3 micron alpha alumina polish, and finally 0.05 micron colloidal silica. Each of the polishing steps were conducted for 1.5 hours at 9 N of force. After polishing, each sample was cleaned under distilled water and dried under a commercial electric hand dryer.

Depending on the method of characterization, samples may have been further etched by 2 % Nital (98 % distilled water, 2% nitric acid). This would allow for increased contrast within the optical microscope and scanning electron microscope. The etching preferentially attacks grain boundaries and specific crystallographic structures and orientations within the sample, leading to heavily etched areas, such as black plessite (described in section 2.3.2) as well as lightly
etched areas, such as the interior of large ferrite plates. Etching was not preformed prior to microprobe analysis or orientational imaging microscopy. Due to oxidation of the sample surface, repolishing was often necessary.

A.2 LIGHT MICROSCOPY

Light microscopy images were obtained using an Olympus VX60M microscope equipped with a ZEISS AXIOCAM MRC 10x video camera. This camera was connected to a computer for analysis and storage of digital images, such as the one shown in figure A.1.

Figure A.1: Light microscope image of a plessite pool in the Cape York meteorite, which includes many plates of secondary Widmanstätten ferrite. This plessite region is bordered by large plates of primary Widmanstätten ferrite.

The use of digital images allows for the creation of a montage, the assembly of many digital images to create a map of the sample surface. An example of a montage is shown in figure A.2, where 420 light microscope images
were combined to create an overall image of the sample surface. The assembly of these images was conducted in Adobe Photoshop.

Figure A.2: Montage of 420 light microscope images of the Cape York Meteorite.

A.3 SCANNING ELECTRON MICROSCOPE (SEM)

Each sample was prepared for the scanning electron microscope as prescribed earlier. However, the samples must be grounded to eliminate the build-up of electrons on the sample surface. This phenomenon is known as “charging,” and is alleviated by connecting our metallic samples to the grounded stage of the SEM. This was performed by creating a silver paint connection across the non-metallic Bakelite, from the sample surface to the bottom of the sample mount.
The SEM used was a FEI Quanta 200 Environmental Scanning Electron Microscope (ESEM). The “E” in ESEM tells that this SEM has the capability of low-vacuum mode, however our analysis did not employ this feature. Our analysis used high-vacuum (0.68 torr) with an accelerating voltage of 20-25 keV and a spot size of 3-4 microns. An example of an SEM image is shown in figure A.3.

![SEM image of plessite pool in the Henbury meteorite. Many small plates of Widmanstätten ferrite are scattered throughout plessite field.](image)

**Figure A.3:** SEM image of plessite pool in the Henbury meteorite. Many small plates of Widmanstätten ferrite are scattered throughout plessite field.

### A.4 ENERGY DISPERSIVE X-RAY SPECTROSCOPY (EDS)

The EDS instrument, an Oxford Instruments (model 6650) EDS, was connected to our ESEM. Chemical analysis was performed at specific locations,
chosen in the SEM, through the software packages of the two instruments. A chemical analysis of a region in the Canyon Diablo meteorite is shown in figure A.4. This region, shown in figure A.4a as an inclusion, has a high P concentration shown in A.4b, and therefore we classify it as a phosphide inclusion, or schreibersite ((Fe,Ni)$_3$P).

Figure A.4: a) A SEM image of an inclusion within the Canyon Diablo meteorite. b) An EDS analysis of the chemical composition of this inclusion. We can confirm that it is the phosphide inclusion schreibersite.
It should be noted that the EDS composition of figure A.4b shows the element terbium. This element can be ignored, since its peaks are associated with both Fe and Ni, the two main constituents of the iron meteorite. The terbium level predicted by the EDS instrument is, in fact, an anomaly.

A.5 ELECTRON PROBE MICROANALYSIS (EPMA)

The electron probe microanalyzer required samples of 1 inch diameter, which necessitated the fabrication of different mounts for EPMA analysis. These mounts were created using ground flat samples, secured in a 1 inch ring by epoxy. After the ring was filled with epoxy, the aforementioned metallographic polishing techniques were performed. However, the EPMA requires that a sample is unetched for analysis and therefore, a Nital etch was not used. Furthermore, a carbon coat across the sample surface allowed for maximum conductivity in grounding.

The EPMA model used was a Cameca SX-50, providing a spatial resolution of approximately one micron with accuracy of approximately 1 – 3 % error [1]. The instrument was used for quantitative analysis of the Ni concentration within the sample, either in area scans or line scans. Considering that the concentration was important, standards were used for instrument calibration prior to analysis.

The Ni concentration line scans acquired from the EPMA analysis permitted the accurate determination of the “M-profile,” which is described in detail in section 2.2. Moreover, a large amount of EPMA data for this thesis is
presented in section 2.6, where many Ni concentration profiles across a retained austenite pool are shown.

A.6 ORIENTATIONAL IMAGING MICROSCOPY

The orientational imaging microscope required small samples of approximately 1 inch diameter, but more importantly a thickness of less than 0.5 inches. This required the modification of previously-made samples to fulfill the size requirements. The OIM requires that a sample is unetched for analysis and therefore, a Nital etch was not used. It should be noted that the sample was first etched and a montage was created to serve as a roadmap for OIM analysis. Then repolishing to remove the etch was performed. The montage roadmap was important considering the sample surface was difficult to navigate in the OIM due to distortion from the high angle necessary for analysis.

The Orientation Imaging Microscope (OIM) used a sample that was tilted 70° from the horizontal and therefore the beam hit the sample surface at a 70° angle. The microscope used backscattered electrons to obtain Kossel diffraction patterns through the elastic and inelastic collision of electrons. The diffraction patterns were obtained as the high angle backscattered electrons were collected on a phosphor screen. This resulted in the formation of bands, which are characteristic of the structure and orientation of the crystal in question.

The crystal structures of the phases present are input into a computer to build a library to which collected diffraction indexes will be compared to. Then during collection, the computer can take the diffraction pattern and associate a
phase and an orientation to the diffraction pattern obtained. An example of a
diffraction pattern is given in figure A.5.

Figure A.5: A schematic diffraction pattern. This information can then be used to
find the orientation for the associated crystal in question [2].

The OIM was employed to determine the orientation across differing phases such
as swathing ferrite and Widmanstätten ferrite. This was to determine the
misorientation between the adjacent phases. This information was presented in
section 3.6 of this thesis and images OIM misorientation scans are given in
figures 3.15, 3.16, and 3.17.
References

2. *Pattern Indexing*, in *Instructions for EDAX*, AMETEK.