Determination of the structure-processing-properties relationship of Fe-6.5wt%Si

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Determination of the structure-processing-properties relationship of Fe-6.5wt%Si

by

Chad Macziewski

A dissertation submitted to the graduate faculty
in partial fulfilment of the requirements for the degree of
DOCTOR OF PHILOSOPHY

Major: Materials Science and Engineering

Program of Study Committee:
  Jun Cui, Major Professor
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The student author, whose presentation of the scholarship herein was approved by the program
of study committee, is solely responsible for the content of this dissertation. The Graduate
College will ensure this dissertation is globally accessible and will not permit alterations after a
degree is conferred.

Iowa State University

Ames, Iowa

2019
DEDICATION

I would like to dedicate this dissertation to my wife Brittany and my son Rowan without whose support I would not have been able to accomplish my dream of obtaining my doctorate. I would also like to extend my sincere thanks to all my friends and family for their wisdom and guidance during my time writing this work.
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ABSTRACT

The role of Fe-6.5wt%Si as a soft magnetic material in motor and power generation will continue to increase as power and efficiency demands keep increasing due to high silicon steel’s superior magnetic and electrical properties when operated at high frequencies. However, the presence of brittle phases creates challenges for mass production of the materials and for machining the materials into parts with demanding geometries. Understanding the processing parameters controlling the presence of the brittle phases is necessary to promote high silicon steels as the superior soft magnetic material. This research pioneers the use of in-situ cooling rate thermal imaging analysis and a 2D Laue x-ray detector to quantify the relationship among processing parameters, final microstructure of melt-spun ribbons and the associated physical properties. These techniques reveal the superlattice peaks of the ordered B2/D03 phases separating them from the background A2 phase. Utilizing a variety of techniques investigating mechanical, electrical, and magnetic properties’ correlation to crystal structure alongside processing parameters a time temperature transformation curve can be generated.
CHAPTER 1 INTRODUCTION

Over the past twelve decades, iron silicon alloys have been the soft magnetic material of choice for energy conversion and energy transportation applications. The combination of readily available constituents combined with the improved performance over other options has led to it being an industry staple. The first experiments on augmenting pure iron at the turn of the 20th century attempted to explore the possibility of finding a superior soft magnetic material. The addition of silicon to pure iron produced a soft magnetic material with less coercivity and higher permeability at the cost of only a fraction of the magnetic strength of pure iron. This suited it for use in transformers as a material that could be easily magnetized and demagnetized at high frequencies. As demand for more efficient transformers rose with the growth of a modernizing society so too did interest in iron silicon alloys. The industry standard was set with iron 3.5wt% silicon, commonly known as electric steel. This material was easy to work at low temperatures and could be readily processed into a variety of shapes. Further research was done to explore what effect adding even more silicon would have. At concentrations above 4.5wt% silicon the material begins to show a brittle behavior at room temperature and requires significant heating in order to be forged. Increasing the silicon concentrations to 6.5wt% yields a material with exceptional soft magnetic materials properties such as very low coercivity, even higher permeability and experiences almost no magnetostriction. These improvements come at the cost of mechanical workability. This increases the production cost of the materials and has been the main reason that while this material has better magnetic properties it was not feasible to use at the time, however, with the increasing demand for higher power density motors and more efficient energy transformation this once overlooked material is poised to make a comeback. The main hurdle to overcome is knowing exactly what processing parameters are necessary to achieve the desired final product.

1.1. History of Fe-6.5wt%Si and its use as a soft magnetic material

The history of Fe-6.5wt%Si begins back at the turn of the 20th century. The original discovery was made by Hadfield when testing which elements when alloyed with iron would produce superior magnetic materials. An ideal soft magnetic material is characterized by having the following properties; relatively high magnetic saturation, low coercivity, high permeability, small
hysteresis. Having a combination of these properties yields a magnetic material which is highly responsive to applied fields, in either direction, and can rapidly change its polarization to match. His original experiments tested a handful of elements (carbon, silicon, nickel, and aluminum) all of which appeared to decrease the alloy’s magnetic strength to varying degrees when compared to pure iron. Some of the elements had positive effects on the other soft magnetic properties such as coercivity and permeability. Most notably of these was silicon which in small amounts produced an exceptional soft magnetic alloy. Though these gains came at a cost to the materials mechanical workability. Concentrations of silicon higher than 3.5wt% began to exhibit extremely brittle behavior, and while having superior soft magnetic properties were ignored due to the increased cost of manufacturing. Thus 3.5wt%Si steel was the gold standard for soft magnetic material applications for much of the 20th century.

As time progressed energy demands in the world kept increasing and with those demands the ability to effectively transport energy from place to place would require high voltage AC power lines and at each point where the energy would be stepped down to useable household levels a transformer was required. The ideal material for transformer cores is a soft magnet, however, as efficiency demands kept increasing better magnets were needed to keep up. One the ways to increase efficiency in transformers is to look at where energy is being lost. The main losses in a transformer are from internal hysteresis loss and eddy current loss. While hysteresis loss can be reduced by reducing the coercivity and increasing permeability these gains are constant at every frequency of operation. Whereas if eddy current losses are greatly affected by operating frequency. If a magnetic material is subjected to very high AC frequency, then the corresponding eddy current losses will dwarf those of the internal hysteresis loss. Lowering the eddy current losses of a material can be achieved by either reducing the thickness of the material below the skin depth of the eddy currents or by increasing the resistivity of the material thereby inhibiting the strength of the eddy currents. The first solution can be applied without changing the chemistry of the currently used electric steel and simply laminating the layers of a transformer core, a process that is currently employed. In order to achieve the second reduction in eddy current losses a change in the chemistry of electric steels is required. It just so happens that when increasing the concentration of silicon in electric steels the resistivity also increases while keeping relatively the same coercivity and permeability. The only problem once again appearance of the brittle phase.
Understanding the brittle phase and its appearance at higher silicon content is the key to utilizing 6.5wt%Si steel effectively. The ductile phase present in the lower silicon concentration steels is a BCC structure (A2) with iron and silicon atoms sitting randomly on each site. Higher concentrations of silicon lead to a more ordered phase (B2) which is still BCC but with the silicon atoms sitting preferentially on the center sites. Finally, at the highest concentrations the silicon further orders and begins to form a structure comprised of eight BCC unit cells where the silicon atoms sit preferentially at the center of half the cells (D03). While there is not enough silicon to fill each of the center sites of either the B2 or D03 structure fully it is a mix of the two phases at 6.5wt%Si. It is the more ordered phases of B2 and D03 that are thought to be the cause of the brittleness present in high silicon steels. Bypassing these brittle phases are necessary if Fe-6.5wt%Si is to be adapted as the primary soft magnetic material for transformer cores. Given that the A2 phase is present at high temperatures (>900 ºC) in high silicon steels it is possible that trapping the metastable phase is possible by using rapid solidification techniques. The most promising of these techniques for industrial applications are melt-spinning and strip-casting. However, it is unknown currently exactly what conditions are necessary to bypass the brittle phase with the least amount of effort. Other methods of processing can be applied for specific applications such as various deposition and diffusion methods for thin sample preparation, but would unlikely be suitable for economical large scale production.

Beyond applications in power transformers high silicon steel could be used in a number of other ways. Inverters, converters, and frequency modulators are all applications that fall under the umbrella of energy conversion as well. In addition, electric generators and motors can be constructed using electric steels for the soft magnetic components. The induction motor in particular is an area of great interest as they provide much more control over speed variability compared to permanent magnet motors and consist of a high percentage of soft magnetic materials either in the stator or the rotor. Sensors provide another alternative use as they require materials which can quickly detect measure and transmit signals. The rapid response time of soft magnetic materials to applied fields of any magnitude makes them ideal for use in electromagnetic sensors, Hall Effect sensors, magnetoresistive effect sensors, etc. The quick response to applied fields can also be used to shield other components from electromagnetic interference. Finally, many electronic components use soft magnetic materials from data storage read and write heads to inductors, switches, and amplifiers.
This is only a brief overview what Fe-6.5wt%Si has to offer. With its exceptional soft magnetic properties and unique physical properties, it is definitely a contender for overtaking conventional Fe-3.5wt%Si as the soft magnetic material of choice for industrial and consumer applications. Each of these types of application is further discussed along with an in depth look at the history of Fe-6.5wt%Si in Chapter 2.

1.2. Effect of Wheel Speed on Magnetic and Mechanical Properties of Melt-spun Fe-6.5wt%Si high silicon steel

Looking at how controlling the ordering of silicon in Fe-6.5wt%Si steel effects the mechanical and magnetic properties is an important step in developing it as commercial soft magnetic material. When subjected to a rapid solidification technique such as melt-spinning it is possible to bypass a brittle phase present in high silicon steels. The effects of this rapid solidification also effects the overall magnetic and mechanical properties, by understanding this relationship it is possible to tune the properties of the melt-spun ribbon to those that are ideal for both workability and performance in operation.

The first step is to subject the material to different processing parameters and measure its response. The easiest way to do this via melt-spinning is by changing the speed of the copper cooling wheel. A series of ribbons were produced using the following wheel speeds; 1 m/s, 3 m/s, 5 m/s, 7 m/s, 10 m/s, 20 m/s, and 30 m/s. Upon initial inspection the ribbons from 10 m/s - 30 m/s looked roughly uniform and each was sufficiently supple. While those from 1 m/s - 7 m/s were somewhat irregular and at extremely slow wheel speeds failed to produce much ribbon. The samples were then subjected to a series of tests to observe both their microstructural, magnetic and mechanical properties.

The microstructural effects where observed by polishing the wheel side of the melt spun ribbon and using a dilute etchant to reveal the grain structure. A good correlation was shown between wheel increasing wheel speed and decreasing grain size. This agrees with intuition as a higher wheel speed should result in less time for the material to grow grains before completely cooling. The relationship between grain size and wheel speed is observed to be quite linear when looking at wheel speeds from 30 m/s – 7 m/s below this speed the trend deviates from the expected linear
reduction and most likely was caused by the instability of the melt pool and the inhomogeneity of the ribbon.

The magnetic effects were measured using a vibrating sample magnetometer (VSM). Samples were loaded by stacking ribbons onto one another and affixed to a magnetically inert sample holder. Each sample was measured with an applied field of 80 kA/m applied field and found that the magnetic saturation (Ms) of each sample was mostly unchanged. This most likely is due to each once containing the same chemistry. While their Ms may not have been heavily altered by the wheel speed their permeability or ease of magnetization appears to have been altered. Higher wheel speeds appeared to have higher permeability with lower wheel speeds again having lower permeability. This may be caused by the absence of ordering in the crystal structure.

The mechanical strength of the sample was measured using nanoindentation and resulted in showing that at high wheel speeds above 10 m/s the samples had a decreased young’s modulus and Vickers’ hardness. This is indicative of higher ductility and the absence of the brittle phases B2, and D03. Though the standard deviation was quite large on some of the samples suggesting that the measurement is highly dependent on the local microstructure.

Finally, the microstructure was measured using a single crystal x-ray diffraction setup with a Mo source and a 2D detector. The ordering of each sample was found by looking for the superlattice peaks of the B2 and D03 phases. A low wheel speeds these superlattice peaks were visible below the (110) rings common between the A2, B2, and D03 phase. At speeds around 7 m/s – 10 m/s the rings started to become faint and by 20 m/s – 30 m/s are completely gone. This type of relationship is consistent with the previous data showing that as wheel speed increases ordering is suppressed in the melt-spun samples. Each of these phenomena including microstructural and mechanical properties are further discussed in Chapter 3.

1.3. Effects of Melt-spinning on Material Properties of Fe-6.5wt%Si

This work is a continuation of that done in Chapter 3. It focuses on the inspection of electrical, magnetic, and mechanical properties of Fe-6.5wt%Si that were done alongside those of the previous chapter. The goal was to attempt to find correlation between the processing parameter of wheel speed with that of the material properties. The results of each test were also scrutinized for
a correlation between the observed trends and the anecdotal evidence of a shift from a ductile ribbon to a brittle one at lower wheel speeds.

The first test was to inspect the effects of wheel speed on electrical resistivity. The four-point probe method was used to measure ribbons of different wheel speeds. While a general trend of increasing resistivity with respect to decreasing wheel speed was observed, the transition from a brittle phase to a ductile one was strongly correlated to this trend. Though lower wheel speeds could not be tested due to insufficient sample size necessary to conduct the test, in addition, there was significant variability in the results possibly caused by sample geometry and surface texture. Another reason for the lack of definitive shift corresponding to mechanical behavior is that this property is a direct result of the chemistry and is less dependent on the ordering of crystal structure.

The next test was observing the change in magnetic saturation ($M_s$) with respect the wheel speed. The previous test showed a nearly identical $M_s$ for each wheel speed, but upon further inspection there a trend of decreasing $M_s$ with increasing wheel speed. Likely the result of random ordering of silicon atoms on all sites, though more studying is necessary to properly explain this. While a general trend is observed again there is no clear distinction between brittle or ductile ribbons. Again this suggests that $M_s$ is more dependent on the chemistry but that ordering of the silicon atoms does play a part albeit a smaller one.

The final test conducted was to probe the mechanical properties of these melt-spun ribbons. Micro-hardness measurements were taken using a Vickers pyramid tip to create small indentation on the edge of samples suspended in a polymer matrix. The results showed a strong correlation between the observed hardness and the wheel speeds that produced ductile and brittle ribbons. The results appear to show a brittle ductile transition between occurring between 7-10 m/s wheel speeds. Suggesting that at lower wheel speeds a brittle phase is present and is suppressed at higher speeds. This result is the most important as it reveals the first clear transition and provides a qualitative indication of the presence of an ordered brittle phase. More information is needed before it can be determined which phases are responsible for the transition. Further information on each of these experiments can be found in Chapter 4

1.4. Thermodynamic and Kinetic analysis of the melt-spinning process of Fe-6.5wt%Si alloy

The previous sections dealt with the microstructural evolution of Fe-6.5wt%Si after it went through the melt-spinning process. This section will focus on the thermodynamics and kinetics of
that process and what it can tell us about the ordering phenomena occurring within the microstructure. The method that will be used will combine experimental cooling rates, CALPHAD calculations, and domain growth theory.

Samples were produced using the melt spinning process with various wheel speeds. The cooling rates were obtained using a thermal camera to capture the surface temperature of the ribbon at each point during the process. Using multiple frames, a cooling rate could be calculated for the ribbon while crossing the phase boundary between A2, and B2/D03. After cooling samples were prepared for dark field TEM imaging. These images were used to measure the antiphase boundary size of the melt-spun ribbon and completed the experimental portion of the experiment.

The next step was to develop a model for the thermodynamic and kinetic analysis of the process. Examining the process of melt-spinning there are two areas sources of cooling present, conductive cooling (ribbon in direct contact with the wheel), and radiation/convection (free flight of the ribbon after leaving the wheel). During the first stage of melt-spinning it is a mixed method of both solidification and cooling occurring, while the second half only incorporates cooling. Depending on the rate of cooling the microstructure will either consist of purely silicon rich A2 phase or a mix of A2, B2, and D03 phases. After setting up a model to predict the atomic motilities of the species Fe and Si. Using these atomic mobility parameters, a simulation for solidification at each wheel speed was conducted and the time for each controlled such that total solidification of the experiment occurred. From these experiments it was shown that upon solidification the B2 phase never forms, only the A2 phase forms. In order for B2 to form it must do so during the cooling stage of the melt-spinning process.

The second half of the process was then modeled assuming no composition change, when it cools below the A2/B2 boundary a secondary-order transition occurs and the B2 phase begins to appear as an antiphase boundary. By measuring the predicted domain sizes and setting the model to match a single experimental data point’s domain size and cooling rate it was shown that the used cooling model matched experimental data quite accurately. Further details of the modeling process are discussed in Chapter 5. The models presented in this section were developed by Dr. Senlin Cui and Professor Valery Levitas.
1.5. In-situ cooling rate analysis of melt-spun Fe-6.5wt%Si

Studying the effects of wheel speed on the final microstructural evolution of electric steels is the first step in determining the critical processing parameters. While this method can lead to control parameters that will repeatedly bypass the brittle phases B2 and D03 it remains valid only for a specific process. The preferred method would be to directly measure what is taking place during this highly energetic process. To that end, it is necessary to measure the amount of cooling experienced during the melt-spinning process. Since measuring temperature changes with standard equipment like thermocouples and optical pyrometers cannot be accomplished due to the dynamic nature of melt spinning, an alternative approach much be considered. The ideal solution would capture multiple data points throughout the process and be able to sample quickly, due to only having a 3-4 second time window. A high frame-rate thermal imaging camera fits all the criteria with the added benefit of being able to record the entire time of flight through the critical temperature ranges.

The setup for these experiments is to view from a head on perspective the ribbon as it contacts the cooling wheel and then passes through to the collection tube. The thermal camera collected several frames of complete data and those were averaged together to create the cooling profile for each wheel speed. A clear trend between faster cooling rates and higher wheel speeds was observed with the critical cooling rate for B2/D03 suppression being between seven to ten meters per second. Using this technique it is possible to accurately measure the surface cooling rate of melt-spun ribbon during stable stream conditions. While this cooling rate is not exactly the precise cooling rate experience by the entire sample it is close to the slowest cooling rate of the entire sample. This is due to the extreme conductive cooling experience by the wheel side of the ribbon while the free side is only able lose heat by radiation and convection. This cooling rate is process independent and can be applied to a variety of manufacturing techniques. More information pertaining to the techniques used in this method can be found in Chapter 6.

1.6. Determining B2-D03 Ordering in a Fe-6.5wt%Si Alloy

Looking at the critical cooling rate is the first step towards building the foundational knowledge for processing Fe-6.5wt%Si. The next step is to determine what microstructural changes that critical cooling rate elicits. Traditional methods of crystallography inspection have been applied to the melt spun ribbon, however, there are a few complications when determining
the final phase composition. The three phases present in Fe-6.5wt%Si are A2, B2 and D03. A2 is a body centered cubic phase with random distributions of iron and silicon. B2 and D03 are a similarly body centered cubic structure where the only differences are the locations of the iron and silicon atoms on the lattice. The B2 structure favors the silicon sitting at the center sites of the cell, and the D03 structure is just eight of the B2 unit cells with silicon favoring only half the center sites. This introduces the first complication with all three structures being body centered cubic in nature their characteristic peaks will overlap making identification of any changes difficult. Secondly, the super lattice peaks formed by the ordering of the silicon atoms in B2 and D03 will appear strongest at low angles. The intensity of the super lattice peaks is much weaker than the characteristic peaks of a BCC structure and therefore will be harder to identify from the background. Finally this material is a melt-spun ribbon containing a metastable phase trapped at room temperature, meaning that post processing must be kept to an absolute minimum in order to not affect the final microstructure.

Taking all of the previously mentioned complications into account the method of selection for determine the ordering present can begin. Traditional X-ray diffraction using a standard setup of Bragg-Brentano geometry with a single point detector will provide incomplete data due to the highly textured nature of the melt-spun ribbon. The solution to this problem is to use a 2D detector and rotate the sample during test to ensure that every orientation is seen. Next, the presence of iron in the sample means that using the commonly available copper X-ray tubes is less than ideal for two reasons. The first stems from the characteristic radiation fluorescence that occurs when iron is struck with copper radiation leading to a high background radiation. The second is that this higher background is strongest at the lower angles and will make identifying the superlattice peaks more difficult. The solution is to use a Mo radiation source to reduce the background fluorescence. Both of these solutions can be accomplished using a single crystal x-ray diffractometer with a molybdenum source and 2D detector. Afterward, integrating the signal captured on the 2D detector will yield the equivalent x-ray diffraction pattern which can then be analyzed to study the peak to peak ratio of superlattice peaks to the (110). More information related to the determining of the phases present can be found in Chapter 7.
1.7. Construction of the TTT Curve

Combining the techniques used in determining the cooling rate of the melt-spun ribbon and the ordering present after melt-spinning/annealing a new tool for processing Fe-6.5wt%Si can be constructed. A time temperature transformation (TTT) curve from this data will allow for future processes to predict and even select a cooling/heating regimen to achieve a desired microstructure. With the previously defined properties of melt spun ribbon this curve would serve as a complete guide between the processing parameters, microstructure, and material properties of high silicon steel. The top end of this curve is constructed by identifying the transition temperature where the crystal structures of interest begin to form. This is predefined by the traditional phase diagram, and while there will be a certain amount of curvature to the nose of the TTT curve a definitive shape is difficult to produce given the amount of uncertainty in the phases present. The bottom half of the curve is constructed by taking a sample which has been subjected to the highest cooling rate possible in order to achieve a completely random distribution of iron and silicon atoms. Afterward, the material is put through a series of annealing steps taking from room temperature heating it and holding at temperature then letting it air cool. The evolved microstructure is then used to define the boundaries of a fully randomized A2 sample and one that has begun to order back into the B2 and D03 phases. The combination of both sets yield the final TTT curve. More information regarding the steps taken to generate the curve can be found in Chapter 8.
CHAPTER 2 A REVIEW OF FE-6.5WT%SI HIGH SILICON STEEL – A PROMISING
SOFT MAGNETIC MATERIAL FOR SUB-KHZ APPLICATION
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Abstract
To meet the growing need for energy efficiency in power electronics and electric machines, a
number of new soft magnetic materials are being investigated. Among them, high silicon Fe-Si
alloy has been recognized as a promising candidate for low-to-medium-frequency applications.
Compared to the currently most widely used 3 wt% silicon steel, the steel containing 6.5 wt% Si
possesses more favorable properties, including high electrical resistivity, good saturation
magnetization, and near-zero magnetostriction. However, the high silicon content facilitates the
formation of ordered phases, resulting in severe brittleness that prohibits mass production using
the economical conventional processing methods. A number of new processing routes have been
investigated and inspiring progress has been made. Prototypes of motors and transformers using
high silicon steel have been demonstrated with improved efficiency and power density. If the
processing cost and limitations of size and shape are properly addressed, high silicon steel is
expected to be widely adopted by the industries. Among all the investigated processing techniques,
rapid solidification appears to be the most cost-effective method for mass producing thin sheet of
high silicon steel. This paper reviews the current state-of-the-art of the Fe-Si based soft magnetic
materials including their history, structure, properties, processing, and applications.

2.1. Introduction
Soft magnetic materials are the materials that can rapidly switch their magnetic polarization
under a small applied field. They are usually characterized by an intrinsic coercivity of less than
1000 A/m. Soft magnetic materials are used for power generation, condition, transfer, and
conversion, and are extensively used in electric machines, power electronics, sensors, and
electromagnetic interference (EMI) preventions. They play a vital role in today’s energy-use
sectors of the economy.
Soft magnetic materials are used in both DC and AC applications. In DC applications, a desired magnetic flux is generated when the soft magnetic materials are energized with an externally applied field, which is normally created by passing an electric current through an excitation coil. After the work is complete, the soft magnetic materials are demagnetized by removing the external field, i.e., by switching off the current in the excitation coil. Examples of typical DC applications are lifting electromagnets or electromagnetic switches. Permeability, magnetic flux density, and intrinsic coercivity are the key figures of merit in DC applications. In AC applications, the soft magnetic materials are magnetized and demagnetized repeatedly following the frequency of the alternating current supplied to the induction coil. Transformers, generators, and electric machines are all operated in AC conditions. In addition to sufficient magnetic flux density, minimum energy loss is the most important consideration in AC applications.

Typical energy losses and their distribution in a 50 HP motor are shown in Figure 2.1. One of the major energy losses directly related to soft magnetic materials is the iron loss, which increases with excitation frequency. For motors and transformer applications, a higher frequency is preferred because it can significantly improve power densities, as shown in Figure 2.2. This is why reducing the iron loss at higher excitation frequencies is a major focus for most of the researchers on soft magnetic materials. The improvement of magnetic material properties is highly rewarding. For example, in a transformer, an increase of 1.5% in energy efficiency implies a direct saving of $240 \times 10^9$ kW·h [1], which is equivalent to $12$ billion/yr for electricity price of $0.05$/KW·h.
Figure 2.1. Typical energy losses and their distribution in a 50 HP motor [2].

Figure 2.2. (a) Plot of power density vs frequency for a motor. (b) Comparison of power densities of a low-frequency motor/transformer and a high-frequency motor/transformer. The size is significantly reduced by the use of high frequencies in both cases [3, 4].

There are two main approaches to minimizing the AC iron losses according to the classic eddy current theory: (1) decreasing the part’s thickness and (2) increasing the part’s electrical
resistivity. The traditional approach is to reduce the sheet thickness to 0.65–0.35 mm [5] [6], and then coating the sheet with an electrically insulating layer. The resulting product is a stack of thin laminates insulated from each layer, which satisfies both the low thickness and high resistivity requirements. Further reduction of the thickness to below 0.1 mm to meet the requirements of aircraft and aerospace applications [7] is possible [5] [8, 9] [10] but not popular owing to the high processing cost and low stacking efficiency [10]. With the low-thickness approach reaching its practical limit, minimization of iron loss demands new soft magnetic materials with a high electrical resistivity. In addition to reducing the thickness and increasing the resistivity to minimize the classical eddy current loss, AC iron losses can also be lowered by tailoring the anisotropy and magnetization reversal processes, including domain wall engineering [11, 12] and refinement of various structure parameters (e.g., impurities, defects, grain size [13], residual stress [14-16], and crystallographic texture [7, 17]). Advanced and sophisticated metallurgical and manufacturing processes are usually required to maintain a low AC iron loss [5, 18].

Besides high electrical resistivity, a high saturation magnetic flux density is also important. At a fixed frequency, a high magnetic flux density implies a high power density and high torque for motor application. With the increasing demand for higher performance, history has witnessed the invention of a variety of soft magnetic materials from mild steel around 1880 to silicon steel in 1900 [19], permalloys in 1915–1923 [20], ferrites in the 1940s [21], amorphous alloys in 1967 [22], high silicon steel in the 1970s [23], and nanocrystalline alloys in 1988 [24]. Soft magnetic materials are categorized into different subgroups based on their chemistry and composition. Typical soft magnetic materials that are available in the market [6] are pure iron and low-carbon steel, iron-silicon alloys (Fe and up to 6.5 wt% Si), iron-based sintered powders or the so-called powder core (Fe with minor alloying of P and/or Si), permalloy (Fe-Ni) or molypermalloy (Fe-Ni-Mo), permendur or hiperco (Fe-Co-V), MnZn or NiZn ferrites, sendust (Fe-Si-Al), Fe-based amorphous alloys (Fe-B-Si), Co-based amorphous alloys (Co-Fe-B-Si), and nanocrystalline alloys (HITPERM, NANOPERM, FINEMET). A collection of commercially available soft magnetic materials in the form of a toroid is shown in Figure 2.3.

Each type of soft magnetic material has its distinct feature; for example, permalloy is known for its near-zero anisotropy and magnetostriction, and high permeability; however, it has either a low saturation magnetization, or a low electrical resistivity depending on the composition.
Although permendur shows the largest room-temperature saturation magnetization [25], its eddy current loss is high due to its low electrical resistivity. Soft ferrites have excellent electrical resistivity, but also have a low saturation magnetization owing to its ferrimagnetic nature. Silicon steel offers high saturation magnetization and low cost, but its eddy current loss is yet to be improved. The amorphous and nanocrystalline alloys are unique owing to their exceptionally low coercivity and eddy current losses; however, they are extremely brittle and lacks high saturation magnetization [26].

Significant developments have taken place in these materials since their invention. New compositions and new devices along with advanced processing techniques were developed to improve the performance of ferrites [27,28]. Metallurgical advances with focus on optimizing texture, defects, impurities, grain size, and residual stress have been achieved in conventional silicon steel [7, 29]. Key understanding of processing the steel with high silicon content and thinner gauge has been established [30]. And for the amorphous and nanocrystalline alloys, researches on improving saturation magnetization, thermal stability, and anisotropies [31-33] as well as new fabrication methods to integrate the brittle materials into devices are also making steady progresses [26]. Over the last decade, new nanocrystalline alloys with higher saturation magnetization and improved ductility have been developed, such as Nanomet which showed a high saturation magnetic flux density (Bs) of 1.83 T [Magnetic properties of 120-mm wide ribbons of high Bs and low core-loss NANOMET® alloy], and Co based [Nanocrystalline soft magnetic ribbons with high relative strain at fracture] and FeNi [Magnetic and mechanical properties of nanocrystalline Fe-Ni-Nb-B Alloys] based nanocrystalline alloys which showed improved bending characteristics. These newly developed nanocrystalline alloys show great potential, and are on the verge of commercialization.
Figure 2.3. Photo showing a collection of commercially available soft magnetic materials in toroid form. Three differently sized samples are wound with primary (outer, yellow color wire) and secondary (inner, red color wire) windings for magnetic measurement. Note that there are several tiny sharp fragments beneath the nanocrystalline core. The tape shattered into fragments during uncoiling owing to the brittle nature of the nanocrystalline sample.

Among all the soft magnetic materials, silicon steel is still by far the most commonly used material with an annual worldwide production of ten million tons and a market share of 80% [30]. Silicon steel (3.2 wt% Si) is currently the most popular choice for motors and transformers because it offers balanced electrical and magnetic properties, and perhaps more importantly, low cost. It is composed of silicon and iron, two of the earth’s most abundant elements. In addition, the conventional 3.2 wt.% silicon steel has excellent ductility, allowing the slabs coming out from the continuous casting line to be directly hot-rolled into hot-bands with 3 to 5 mm thickness, then cold-rolled into thin laminates of less than 1 mm thickness. Recently, with the market demand of further reduction in energy loss, a new generation of materials such as high silicon steel, amorphous alloys, and nanocrystalline materials have been intensively investigated. Unfortunately, none of these materials possesses all of the desired physical properties and all of them incur high processing
costs. Figure 2.4 and Figure 2.5 compares the saturation magnetization, electrical resistivity, and iron loss of these materials at 1 T and 400 Hz, respectively. These figures show that 6.5 wt% silicon steel offers a good balance of high saturation magnetization (1.8 T) and high electrical resistivity (82 $\mu$Ω-cm), and low iron loss. In addition, high silicon steel displays near-zero magnetostriction [34], which is necessary for reducing the operating noise of transformers.

Figure 2.4. Comparison of electrical resistivity and saturation magnetization of a few key soft magnetic materials [9, 31, 35-40].

Figure 2.5. Comparison of iron loss W10/400 (a) and magnetostriction (b) of a few key soft magnetic materials [9, 31, 35-40]. Note that the magnetostriction of 6.5 wt% Si steel is too small (0.01 ppm) to be shown.
Despite these favorable properties, the application of high silicon steel remains mostly at the lab scale [41]. The main hindrance to its wide application is its high processing cost resulting from its brittleness. The material cannot be mass-produced using the economic cold roll process, which is widely used for low silicon steel. A majority of research conducted in the field of high silicon steel focuses on resolving the brittleness problem while maintaining and enhancing its magnetic properties. This paper reviews the history, structure, properties, processing, and applications of high silicon steel.

2.2. History of high silicon steel

The beginning of silicon steel started at the turn of the 20th century when the developing world was expanding, and with it, the demand for the generation and transportation of electrical energy was increasing. An English scientist named Robert A. Hadfield began investigating methods to improve the soft magnetic material of choice at that time: pure iron. He began by introducing various elements, creating several iron alloys, and observing the effects of alloying elements on its magnetic and electrical properties. He began looking at carbon, aluminum, nickel, and silicon. The majority of these additions sacrificed much of the material’s magnetic saturation without imparting enough beneficial effects. However, silicon, while still decreasing the overall magnetic strength, was able to dramatically improve the magnetic permeability, and electrical resistivity, while decreasing the coercivity [19]. His findings were further investigated by Guimlich in 1912 and Campbell in 1920, who confirmed that the addition of up to 6.5 wt% silicon yielded the best electrical and magnetic properties [42, 43]. The only drawback to this addition was that above 3.2 wt% silicon, the material becomes brittle and difficult to work with using the traditional manufacturing methods. Therefore, for the time, 3.2 wt% silicon became the gold standard of soft magnetic materials.

Around 1930, Norman P. Goss was looking into ways to further improve the 3.2 wt% silicon steel, which were then used in the American electrical grid. The original method for processing the material left it with isotropic properties with a random orientation of grains. The crystal structure of silicon steels has an easy magnetic direction of \( <100> \), a medium direction of \( <110> \), and the worst direction of \( <111> \). Goss developed a method of orienting the silicon steel grains with a \( <100> \) texture, such that the subsequent processing would selectively encourage their
growth and result in grain-oriented silicon steel. The grain-oriented silicon steel exhibited increased permeability and a significant reduction in iron loss in the rolling direction, perfect for high-voltage power transformers [44].

As the demand for more powerful and efficient means of producing 3.2 wt% silicon steel increased over the next 40 years, much of that time was spent refining various processing techniques in an attempt to extract as much performance as possible. Beginning around the 1970s, the demand for a soft magnetic material with exceptional electrical resistivity for high-frequency audio equipment brought 6.5 wt% silicon steel back into the limelight. Its inherently higher electrical resistivity and near-zero magnetostriction made it a perfect material for applications at high frequencies as it could minimize losses from both eddy current loss and shape changes [23]. This sparked a renewed effort to find alternative ways to process the brittle material, and many methods were tested over the next few years including melt spinning, chemical vapor deposition (CVD), twin rolling, and powder metallurgy [45-48]. Melt spinning showed great promise in producing a low-cost 6.5 wt% silicon steel [49-51]. As demonstrated by Liang et al. [51], 30-mm-wide continuous tapes could be successfully produced by melt spinning, and their excellent ductility ensured that the tapes could be coiled into spools. However, the industry did not switch over immediately to 6.5 wt% silicon steel due to the increased cost, and it is only with the recent demand for even more efficient electric motors and high-voltage transformers that the high silicon steel is finally on the verge of being accepted as a commercially viable soft magnetic material [51].

2.3. Structure of high silicon steel

2.3.1. Effect of silicon in steel

Silicon addition in steel has several profound effects. Due to the smaller atomic radius of Si (1.11 Å) than that of Fe (1.26 Å), the lattice parameter of Fe-Si decreases linearly from 0 to 18 wt% of silicon content [34, 52]. A change in slope occurs at around 5 wt% of silicon that corresponds to the ordering, as will be discussed in detail below. The density of Fe-Si follows the same trend as that of the lattice parameter, and Fe-6.5wt%Si has a density of 7.48 g/cc [34].

Silicon addition rapidly increases the electrical resistivity of iron [52]. The electrical resistivity of 6.5 wt% Si steel is 82 μΩ-cm, while that of pure iron is 10 μΩ-cm [7, 34]. Arato et al. [53] found that Si addition increases the electrical resistivity linearly with a coefficient of 11.62
\(\mu\Omega\)-cm per wt% in the range of 0.15–2.2 wt% silicon steel. A similar coefficient of 12.785 \(\mu\Omega\)-cm per wt% was measured by Hou [54] with the silicon content ranging from 0.21 to 2.0 wt%. In practice, the silicon content was back-calculated by measuring the electrical resistivity by NKK corporation in the production line due to the near-linear relationship between resistivity and silicon content over the range of 3–8 wt% [35]. The increase in electrical resistivity results in lower eddy current loss [8, 34, 55] and higher efficiency. Ruder found that steel with 6.5 wt% Si has the lowest total loss at 1 T magnetic induction and 60 Hz induction frequency [56].

The magnetocrystalline anisotropy also decreases with silicon addition [7], thus resulting in higher relative permeability for high silicon steel [1]. The relative permeability was shown to increase slowly below 3 wt% silicon, then increase rapidly reaching a maximum of 29,000 at around 6.5 wt% silicon content before it drops [34]. The magnetostriction decreases rapidly along the \(<100>\) axes with increasing silicon content, while it increases slowly along the \(<111>\) axes, resulting in nearly zero combined magnetostriction for 6.5 wt% silicon steel [34, 35, 57]. The minimum magnetostriction can effectively reduce the transformer noise [57]. The saturation magnetization, however, decreases with increasing silicon content, reaching \(\sim 1.8\) T at 6.5 wt% silicon [7, 34]. In addition, the materials become more brittle with increasing silicon content due to the formation of ordered phases.

### 2.3.2. Ordering in high silicon steel

Fe-Si electrical steels have a substitutional A2 body-centered cubic (bcc) structure at low silicon concentrations. When the silicon concentration is increased to about 5.3 wt%, B2 ordering starts to occur below 500°C according to the phase diagram shown in Figure 2.6a [58, 59]. D0\textsubscript{3} ordering starts to appear when the silicon content is increased beyond 6 wt%. The terms A2, B2, and D0\textsubscript{3} are Strukturbericht symbols that specify the structure of a crystal, and represents monatomic bcc \(\alpha\)-Fe, CsCl-type AB compounds, and AlFe\textsubscript{3}-type \(A_\text{m}B_\text{n}\) compounds, respectively. The ordering of Fe-Si can be best described using the superlattice structure consisting of four interpenetrating face-centered cube (fcc) cells having a lattice parameter twice that of a single bcc cell [59], as depicted in Figure 2.6b.

The superlattice structure can also be viewed as consisting of 8 bcc lattices stacked as a cube. A2 is in the disordered state, with random distribution of iron and silicon atoms in the
The unlike-atom pairing of the nearest-neighboring atoms results in B2 ordering, where the sublattice sites are preferably occupied by silicon atoms. Further ordering between the next-nearest-neighboring atoms results in D0₃ ordering, where only half of the sublattice sites with the longest separation are preferably occupied by silicon atoms. It should be noted that the full B2 structure requires all sublattice sites (bcc sites) to be occupied, corresponding to the stoichiometric compound FeSi. Fe-6.5wt%Si has insufficient silicon to form the stoichiometric compound. The B2 phase in Fe-6.5wt%Si adopts the structure, wherein silicon atoms occupy some of the sublattice sites (bcc sites) and iron atoms fill rest of the sites. Similarly, the full D0₃ configuration requires 4 silicon atoms and 12 iron atoms, which correspond to the stoichiometric compound Fe₃Si. The D0₃ structure in Fe-6.5wt%Si represents the structure in which silicon and iron tend to occupy the sites in the same manner as they do in Fe₃Si D0₃.

Due to the ordering, additional dots or lines appear on the electron or X-ray diffraction patterns [60]. These superlattice dots or lines are used for material characterization to determine the presence of B2 and D0₃ phases. D0₃ generates a unique superlattice peak corresponding to the \{111\} planes, while B2 shares the \{200\} superlattice peak with the D0₃ \{100\} planes. The ordering interacts with dislocations resulting in a strengthening effect [61], which adversely affects the mechanical properties. Superdislocation slip deformation mechanism as proposed for B2 and D0₃ lattices [62] also deteriorates the mechanical properties. B2 and D0₃ ordering leads to improved magnetic properties, where B2 growth is responsible for higher specific magnetization, and D0₃ growth is responsible for low magnetostriction, high maximum permeability, and low coercive force [63].
Figure 2.6. (a) Fe-Si phase diagram of high silicon steel [58, 59]. (b) Superlattice crystal lattice of high silicon steel. For disordered A2 phase, Fe and Si can sit in any of the plotted sites. For B2, Fe prefers the sites denoted by solid black dots and gray dots, while Si prefers the sites denoted by gradient dots and open dots. For D0\textsubscript{3}, Si prefers the sites denoted by open dots, while Fe prefers all the other sites.

2.3.3. Suppression of ordering in silicon steel

To suppress the deleterious ordering, a variety of fast quenching routes has been explored. Raviprasad et al. [64] examined the ordering of rapidly solidified Fe-6.5wt%Si by three processing routes: planar flow casting (PFC), melt spinning (MS), and twin rolling (TR). TEM analysis revealed that B2 ordering can be found in the single-roll-processed (PFC and MS) samples, while the additional D0\textsubscript{3} ordering can only be found in the twin-rolled samples. In addition, the B2 domains were also found to increase from 20–30 nm in the PFC and MS samples to 60 nm in the TR sample. This study suggested a strong dependence of ordering on cooling rate. The typical tangential wheel speeds used by these techniques were 8–60, 42, and 32 m/s, respectively. But, the actual cooling rates associated with each wheel speed for each method were not investigated.

The cooling process using three quench media was studied by Zhang et al. [65]. The cooling rates of oil, water, and salt water (10% NaCl) were found to be 74, 304, and 375°C/s, respectively, for the samples with dimensions of 2 mm×5 mm×35 mm. The faster cooling rates
resulted in a reduction of the ordered region with the domain sizes changing from 1–3 μm to 20–200 nm and 5–50 nm, respectively. However, a higher cooling rate was found to create larger residual tensile stress, which to certain degree, diminishes the ductility gained by lowering the degree of ordering.

Fu et al. [62] studied the effect of cooling rate on Fe-6.5wt%Si-0.05wt%B alloy with columnar grains formed by directional solidification. Rapid oil quenching reduces the growth of needle-shaped boron-rich precipitates that are harmful to the bending properties. The size of the ordered phase reduces from 3–5 μm to 20–50 nm, suggesting a reduction in the degree of ordering from furnace cooling to oil quenching.

It appears that rapid cooling can suppress the formation of D0₃ and reduce the size of B2, but cannot completely suppress the B2 ordering [66]. A summary of the relationship between known cooling rate and the resulting ordering is shown in Figure 2.7.

![Figure 2.7](image.png)

Figure 2.7. B2/D0₃ ordering as a function of cooling rate. Red circles indicate the presence of D0₃ phase, and black squares indicate the absence of D0₃ phase. The presence of D0₃ is unknown in the case of blue triangles [65, 67, 68].
In addition to quenching, deformation was also found to have effect in decreasing the ordering and reducing brittleness. Fu et al. [69] found that the superlattice B2 and D0₃ peaks were missing in the TEM diffractions patterns after compressing the sample at room temperature, and the compression deformation allowed the sample to be warm and cold rolled to a 0.2-mm-thick sheet with no obvious edge cracks.

2.4. Properties of high silicon steel

2.4.1. Magnetic properties

High silicon steel can be used in both direct current (DC) and alternating current (AC) applications. Its DC and AC magnetic properties are equally important. Permeability, magnetic flux density, and coercive field are the key properties for DC applications, while iron loss including hysteresis loss, eddy current loss, and anomalous loss are the most important properties for AC applications.

2.4.2. DC magnetic properties

The permeability of hot-rolled and annealed silicon steels with the silicon content ranging from 0.21 to 2.0 wt% was studied by Hou [54]. Grain size was found to be the predominant factor for permeability at a low induction (1T) for both DC and AC 50 Hz conditions. Under a high induction, i.e., 1.5 T, the <200> out-of-plane texture component was found to have greater influence. The magnetic flux density was found to increase with increasing <200> texture component, while the effect of grain size was insignificant. The coercivity is inversely proportional to grain size for polycrystalline magnetic materials with grain sizes above 150 nm following the 1/D law [70, 71]. With decreasing coercivity, the permeability increases, as they are inversely related [71]. Chemistry also plays a role in coercivity. Arai and Tsuya [72] showed that, compared to other compositions, 6.5 wt% silicon steel displayed the lowest coercive field. Further, iron loss occurs in DC application as hysteresis loss as well, but it is generally not a major concern.

2.4.3. AC magnetic properties (iron loss)

Iron loss is one of the most important properties of soft magnetic materials used in AC conditions. Iron loss is the energy loss (in watt/kilogram or watt/pound) per cycle at a specific
frequency and flux density [1]. Iron loss is expressed as “Wa/b”, where “a” is the magnetic flux density in Kilogauss (KG) or one-tenth of a Tesla (T), and “b” is the frequency in Hz. For example, W10/400 denotes the total iron loss at 10 KG or 1 T magnetic induction with 400 Hz frequency.

The iron loss for sinusoidal excitation can be approximated using empirical equation in the form of Steinmetz equation:

\[ P_v = C_v f^\alpha B_m^\beta, \]

where \( P_v \) is the power loss per volume; \( f \) is the frequency; \( B_m \) is the peak magnetic flux density; and \( C_v, \alpha, \) and \( \beta \) are the three fitted so-called Steinmetz parameters. The very first formula derived by Steinmetz does not have the frequency term, and \( \beta \) was determined to be 1.6 for hysteresis losses and 2 for eddy current losses [73]. The three Steinmetz parameters in equation (1) vary for different materials and testing frequencies, and are usually published by soft magnetic material manufacturers for their products. The Steinmetz equation can also be extended into the non-sinusoidal excitation with modification [74-76].

The iron loss can be better understood by the loss separation approach [77]. The iron loss consists of hysteresis loss, eddy current loss, and anomalous loss (sometimes called excess loss), with eddy current loss being the major contributor at frequencies higher than 400 Hz. The contribution of each component as a function of frequency is illustrated in Figure 2.8 [1, 77].

![Figure 2.8. Schematic of iron loss separation as a function of frequency [1, 77].](image-url)
Hysteresis loss per cycle is the energy loss when the material is cycled once between a positive and negative applied field. It is the area enclosed by the B versus H loop. Hysteresis loss can be determined experimentally by the DC magnetic measurement of a single BH loop.

The eddy current loss is created by the electromotive force (emf) caused by the alternating magnetic flux. Its direction is always opposite to the magnetic field, thereby reducing the flux change according to Lenz’s law. Its magnitude is proportional to the change in magnetic flux and the cross-section area of the material. The eddy current generates heat, causing power loss proportional to the square of the eddy current and the resistance. Eddy current loss (classical) can be calculated assuming complete flux penetration and constant permeability, and strongly depends on \( d, f, \) and \( B_0 \). [1]

\[
P = \frac{10^{-9} \pi^2 d^2 B_0^2 f^2}{6 \rho} \text{erg sec cm}^3,
\]

where \( d \) is the thickness in cm, \( B_0 \) is the surface flux density in Gauss, \( f \) is the frequency in Hz, and \( \rho \) is the resistivity in \( \Omega \)-cm. The unit resulted for \( P \) is erg/sec cm\(^3\). It converts to watt/cm\(^3\) when multiplies by \( 10^{-7} \).

Classical eddy current estimation through Maxwell’s equations assumes that the material is completely homogenous and devoid of domains [78]. The existence of magnetic domain structures results in a more complex and non-uniform distribution of eddy currents [6]. The classical eddy current theory tends to underestimate the total iron loss. The excess eddy current loss component that cannot be explained through the classical model of uniform magnetization is called anomalous loss [6]. Since it is merely eddy current loss that is not calculable in detail, some researchers had suggested that the anomalous loss be renamed as excess eddy current loss [78]. A common practice in estimating the anomalous loss (\( P_a \)) is to subtract the hysteresis loss (\( P_h \)) measured under DC condition and the eddy current loss (\( P_e \)) calculated from the classical formula from the measured total iron losses [78]. A more complex evaluation of eddy current loss is presented by Pry and Bean [79] by considering the domain structure effect. The domain model eddy current loss is larger than the classic model power loss, and the ratio between these two values increases with an increase in \( 2L/d \), where \( L \) is the domain size and \( d \) is the sheet thickness. When the domain size is constant, the classic model tends to underestimate more for a thinner sheet [1].
The magnitude of eddy currents is not uniform along the entire specimen. The eddy currents are the strongest at the center, where all the current rings add, and weaken toward the surface [1]. As a result, the H and hence B inside the body can be much lowered than that on the surface, especially in a thick specimen. This causes shielding of the interior of the thick specimen from the applied field, which is called the skin effect. The field, $H_x$, and flux density amplitude, $B_x$, inside the specimen at a distant $x$ below the surface can be calculated using the following equation, assuming that the permeability, $\mu$, is constant everywhere in the specimen and under any field [1].

$$\frac{H_x}{H_0} = \frac{B_x}{B_0} = \left[ \frac{\cosh\left(\frac{2x}{\delta}\right) + \cos\left(\frac{2x}{\delta}\right)}{\cosh\left(\frac{d}{\delta}\right) + \cos\left(\frac{d}{\delta}\right)} \right]^{\frac{1}{2}}$$  \hspace{1cm} (3)

$$\delta = 5030 \sqrt{\frac{\rho}{\mu f}} \text{ cm}$$  \hspace{1cm} (4)

Here, the field is applied parallel to the surface of the sheet and vary sinusoidally with time as $H = H_0 \cos 2\pi ft$, where $d$ is the sheet thickness in cm, $\delta$ is the “skin depth,” $\rho$ is the resistivity in $\Omega$-cm, and $f$ is the frequency in Hz. Skin depth is the depth under the surface where $H_x$ or $B_x$ drops to 1/e (~37%).

### 2.4.4. Iron loss management

Iron loss can be affected by silicon content, grain size, impurities, and texture [80]. Larger grains result in smaller coercivity and higher permeability, both of which lead to lower hysteresis. However, on the contrary, larger grains tend to result in larger eddy current loss and anomalous loss [81, 82]. Shimanaka et al. [8] found that the desired grain size for the lowest W15/50 lies between 100 and 150 $\mu$m for 1.85–3.2 wt% Si, with the high silicon content requiring larger grain sizes. Hou [54] found that hysteresis loss and eddy current loss decrease with increasing silicon content from 0.21 to 2.0 wt%. The reduction in hysteresis loss was mainly due to texture and grain size, and the reduction in eddy current loss was primarily due to the increase in resistivity. For the frequency range of 1–1000 Hz, Campos et al. [82] proposed a model to roughly estimate the optimum grain size, which states that the optimum size is dependent on resistivity, frequency, and
sheet thickness. The optimum grain size of a 0.51-mm-thick electric steel was estimated by Campos et al. to be in the range of 163–110 µm for the frequency range of 30–100 Hz.

Impurities, especially fine particles, results in an increase in hysteresis loss due to the pinning of domain wall motion and grain growth [8]. Carbon and nitrogen are usually reduced to 40 ppm and 20 ppm by moist hydrogen annealing and Al addition, respectively [8]. Reduction in sulfur content from 65 ppm to 4 ppm can also result in a lower hysteresis loss, as shown by Oda et al. [83]. Aluminum addition reduces free nitrogen by forming AlN, which also improves the texture [8]. However, the presence of aluminum oxide particles increases the rate of wear of the punch-out dies [1]. Other alloy additions such as Sb, Cr, and B have been explored. Antimony addition was shown to result in both lower loss and higher permeability [84]. Komatsubara et al. [85] studied 4 wt% Cr addition in 4.5 wt% silicon steel in Kawasaki Steel Corporation. The alloyed steel exhibited good workability owing to its low Vickers hardness of 240 HV and offered lower iron loss at high frequencies over 5 kHz. However, its iron loss at low frequencies including 400 Hz and 1 KHz was worse than that of 3.2 wt% silicon steel and 6.5 wt% silicon steel. Kim et al. [86] showed that boron addition up to 530 ppm into 6.5 wt% silicon steel improved the workability due to grain refinement resulting from boron grain boundary segregation.

Texture also affects the iron loss, with lower loss present in the (100) plane followed by (110) and (111) planes [8], corresponding to the easy magnetization axis of <100> and hard magnetization axis of <111> in bcc iron. Texture can be achieved in electric steel through the following routes: (1) utilizing the γ to α transition (fcc to bcc structure) during cooling [8]; (2) recrystallization and annealing after heavy cold-rolling [1, 8, 87]; (3) rapid solidification [88] [89] [90]; (4) directional solidification/recrystallization [91] [92] [93]; (5) alloying addition [84] [8]; and (6) magnetic annealing [94-97]. The desired texture for the stationary transformer and for the motor are different. For transformers, the field is along the long edges of the laminations. Easy <100> direction in the direction of magnetization is preferred, and the desired texture is \{hkl\}<100>. In practice, grain-oriented steels were so prepared that they have the \{110\}<001> GOSS texture. For motor, the field is in the plane of the sheet, while the angle in the plane rotates. \{100\}<uvw> is satisfactory as it keeps the hard <111> axis out of the plane, and <100> out-of-plane fiber texture is more favorable, as it would be isotropic in the sheet plane [1]. Moreover,
although a cube texture \{100\} \langle100\rangle has been achieved, it has not been produced in large quantity [1].

The anomalous loss is also affected by domain sizes and the number of domain walls [78]. Decreasing the domain size [12] and increasing the number of domain walls reduce the anomalous loss [78]. A number of domain-refining techniques have been proposed to reduce the anomalous loss [12, 78]. Typical methods include grain size refinement, application of stress through coating [98], laser irradiation [99], laser scribing [45], and introduction of local strain [100].

2.4.5. Lamination and near-net shape processing

The effect of thickness on iron loss can be large. Oda et al. showed a 25%–30% iron loss reduction for W10/400 when the thickness of the electric steel was reduced from 0.35 mm to 0.20 mm [101]. Kan et al. [55] also showed similar results for W12.5/50 for ribbons with 100 µm thickness. Due to the skin depth problem, silicon steel is mostly used in the laminated form to reduce energy loss. Thin paper was historically used by George Westinghouse to laminate wrought iron sheets to make transformers in 1885 [102]. Nowadays, a coating is applied to each thin silicon steel laminate for electrical insulation. A few coating strategies are available: organic varnish can be used, but it cannot withstand the stress-relief annealing; a slightly oxidizing annealing atmosphere can be used to form an iron oxide film that tightly adheres on the surface; and MgO powder coating is often used before high-temperature annealing. MgO powder combines with SiO$_2$ to form a glassy magnesium silicate, and puts the steel in tension after cooling to room temperature due to a smaller CTE, which may also result in lower core losses due to the favoring of 180° domain walls [1].

The insulating coating, not being a ferromagnetic material, lowers the effective volume of the electric steel. In addition, the coating and laminating process adds additional labor to the production. Moreover, the magnetic properties including AC loss and magnetizing force H15/50 (H15/50 is the magnetic field required to reach a magnetic induction of 1.5 T at 50 Hz) of silicon steel can be severely affected by the stamping method used to prepare the laminates. According to Kurosaki et al. [103], the strains produced during shearing and laser cutting resulted in higher W15/50 and H15/50 compared to the strain-free laminates obtained by wire electrical discharge machining (WEDM). Subsequent annealing at 750°C for 2 h to relieve stress can be used to
eliminate the difference. The authors also reported that the interlocking and welding used to clamp the laminates led to higher eddy current losses due to short circuits.

Near-net shape processing of insulated electric steel may offer a solution to this dilemma. Composites of insulated soft magnetic materials are often called soft magnetic composites (SMCs). Shokrollachi et al. recently reviewed SMCs [104]. The insulating coating can be organic or inorganic, where the organic coatings typically are epoxy, acrylic, polyester, epoxy-polyester hybrid, and polyurethane, and the inorganic coating can be an oxide (such as Fe₂O₃), a phosphate (such as zinc phosphate, iron phosphate, and manganese phosphate), or a sulfate. SMCs are attractive owing to their low eddy current loss, which is made possible by the high resistivity offered by the inter-particle insulation. Its ability to undergo near-net shape processing via the powder metallurgy compaction route is also an advantage. However, the coating and the air-gap dilute the material’s saturation magnetization and permeability. In addition, higher hysteresis losses are often observed due to the strain produced during the compaction.

Recently, by mixing with a 35 vol% wax-based binder, near-net shaping of an atomized 12.7 µm Fe-6.5wt%Si powder compact was made possible via metal injection molding by Miura and Kang [105]. Followed by solvent debinding, thermal debinding, and 1350°C sintering, a nearly 100% dense body was produced. However, the DC magnetic properties of the sintered compact were not as good as that of the wrought Fe-6.5 wt% alloy. And the iron loss of ~400 W/kg at 10 kHz is high. Such high iron loss was probably resulted from the lack of lamination of the sintered body. In another study, a nearly fully dense Fe-6.5 wt%Si/SiO₂ core-shell composite was synthesized [106]. The process involves ball milling of water-atomized Fe-6.5wt%Si alloy powders and SiO₂ powders followed by spark plasma sintering at 1150°C. The composite has an excellent electrical resistivity of 1400 µΩ-cm. However, both the coated and un-coated Fe-6.5wt%Si compacts suffered from poor DC and AC magnetic properties. A new in situ chemical deposition process using 3-aminoprophyltriethoxysilane (APTES), tetraethyl orthosilicate (TEOS), anhydrous ethanol, and ammonia was used to replace the ball milling process, yielding a remarkably high electrical resistivity of 4800 µΩ-cm [107]. W10/400 of 10.6 W/kg was achieved on a 6.35 mm composites compact, which was similar to that of a commercial thin 6.5 wt% silicon steel sheet [107]. However, the newly produced thin composites had lower saturation magnetization and permeability caused by the addition of SiO₂.
It should be noted that all the conventional bulk magnets use either sheets, or near-spherical powders as building blocks. A new strategy was proposed by Cui et al. using the coated flakes, which offers new method to minimize the saturation magnetization loss while maintaining high electrical resistivity [108]. The flakes can be mass-produced by melt spinning, coated with a nonconductive coating, and then consolidated into bulk magnets with a “brick wall” structure, as shown in Figure 2.9. This strategy uses ductile flakes instead of sheets or powders as building blocks for the bulk magnet. The use of flakes is different from using sheets in that near-net shape processing can be achieved, and differs from using powder of the same thickness in that the demagnetization factor and eddy current can be minimized. A limitation of the flakes approach is the relatively low packing density, which can lead to low density and low magnetization. It, however, offers endless possibilities to optimize the flake size, spacing, and the coating thickness for specific frequencies and induction levels.

![Figure 2.9. Schematic showing a magnetic material consisting of (a) conventional spherical powders and (b) high-aspect ratio flakes. The powders and flakes are in blue and the coating is in gray. For comparison, the thickness of the flakes is equal to the diameter of the powder.](image)

2.4.6. Mechanical properties

Tensile tests performed by Seifert et al. [109] on double-roller-quenched and annealed Fe-6.5wt%Si steel suggested that the appearance of D0₃ superlattice structure is responsible for the loss of ductility. They also showed that the ductile as-quenched samples could be converted into brittle materials by air cooling or annealing, and brittle ribbons can be converted back into ductile
ribbons by annealing above the B2-D0₃ temperature followed by quenching; this further supports the argument that D0₃ ordering renders the Fe-6.5wt%Si steel brittle. Higher bending numbers were observed on thinner samples, and the increased ductility of thinner ribbon was claimed to be caused by the greater mobility of dislocations in the surface region.

The stress-strain curves and XRD patterns of the melt-spun Fe-6.5wt%Si ribbon in the as-spun state and annealed state are shown in Figure 2.10a and Figure 2.10b, respectively. After annealing at 1100°C, the annealed sample was slowly cooled at a rate 10°C/min. The annealed sample exhibited worse mechanical properties than the rapidly quenched sample did, as demonstrated by lower strength and less elongation at break. XRD analysis revealed the formation of B2 and D0₃ in the annealed sample, which is responsible for the loss of ductility. However, as compared to the ductile as-spun state, annealing improves the magnetic properties including relative permeability and coercive force, as shown in Figure 10c. It also reduces the iron loss at 400 Hz and 1000 Hz, as shown in Figure 2.10d. Production in the ductile state followed by a final annealing prior to application is key for the production of high silicon steel with the desired magnetic properties.
Figure 2.10. (a) Stress-strain curves of Fe-6.5wt%Si steel strips tested in as-spun state and annealed state followed by slow cooling at 10°C/min rate. The strain was measured by grip-to-grip separation. (b) XRD patterns of Fe-6.5wt%Si steel in as-spun state and annealed state followed by slow cooling at 10°C/min. The insert shows the superlattice peaks. (c) BH loops for Fe-6.5wt%Si tape-wound core in as-spun state and annealed state tested up to 8000 A/m using KJS Associates/Magnetic Instrumentation Model SMT-700 Soft Magnetic Tester. The inset shows the BH loops with 1 T peak magnetic flux densities. (d) Total iron losses of the Fe-6.5wt%Si tape-wound cores as a function of flux density at different frequencies in the as-spun state and annealed state.

The hardness increases monotonically with increasing silicon content according to Hou [54], who studied steel with a maximum silicon content of 2.0 wt%. Shin et al. [58] studied the hardness of silicon content up to 13 at% by micro-indentation and nanoindentation tests. Vickers hardness was found to vary linearly with silicon content. For high silicon steel, the equation $HV =$
-112 + 41.1 at% Si was established, and for low (less than 6 at%) silicon steel, the equation $HV = 59.9 + 24.3 \text{ (at\%)}^{2/3}$ was found valid. The (at\%)$^{2/3}$ and at% correspond well with substitutional solution hardening and short-range ordering hardening, respectively [110]. Nanoindentation showed two peak values, 5.55 GPa and 6.25 GPa, for the 100 indents made on the sample annealed at 650°C for 2 h and then furnace cooled, which had both A2 and B2; this was the only result that suggested that A2 and B2 phases might have different hardnesses. Haiji et al. [35] showed that the workability can be further improved by suppressing grain boundary oxidation. The presence of oxygen during annealing was shown to reside in the grain boundaries, facilitating grain boundary rupture, which can result in poor workability.

To increase the ductility of high silicon steel, various alloying additions have been explored. Al [111], Ga, Cr, Ni, and Nb were found to increase the plasticity of high silicon steel [112]. However, the amount of alloying additions has to be restricted to a limited quantity, i.e., 2%, or in the case of Nb at 0.5%, due to the adverse effect on magnetic properties [112]. Mn addition was also explored and showed a more prominent effect than Ni in terms of ductility [113]. Kim et al. [86] reported significant improvement in the workability of high silicon steel with the addition of up to 530 ppm boron, which allowed cold working of thin high silicon steel when a careful procedure is followed. Despite the marginal improvement, the alloyed high silicon steels typically suffered from worsening magnetic properties.

### 2.5. Processing of high silicon steel

Due to its brittle nature at room temperature, processing of high silicon steel using the conventional route is not possible. Multiple processing techniques have been developed to mitigate the brittleness problem, including special thermal mechanical processing (combination of hot/warm/cold rolling), rapid solidification, and deposition/diffusion annealing. All these processes are intended to produce thin silicon steel strips that can be laminated for practical applications. A few important properties including coercive force, permeability, magnetic induction, and iron losses at various conditions are summarized in Figure 2.13 at the end of this section.
2.5.1. Thermal mechanical processing

A series of thermal mechanical processing experiments were performed on Fe-6.5wt%Si by various groups, such as Houbaert and Schneider’s group [114-119], Lin’s group [120-122], and others [80, 97, 123, 124]. These processes were possible due to the avoidance of ordering, either by using high temperatures for hot rolling, or quenching prior to the cold rolling runs. Hot rolling of slabs has to be conducted above 1000°C as the mean flow stress was found to significantly increase in high silicon steel when the temperature drops below 950°C, but remains low above 1000°C [118]. In practice, Yanez showed that after heating the slabs to 1150–1250°C, hot rolling in four or nine passes with a total reduction of about 95% is possible with no major problems [118] [115]. Cold rolling was only possible by prior accelerated cooling. With the right processing parameters, a final thickness of 0.4 mm was achieved by cold rolling [115]. However, cold-rolled samples can lose their ductility due to rapid domain growth, and any further rolling was not possible [115]. Industry prefers hot and cold rolling processes because of minimum changes to the current low silicon steel production lines.

Another rolling technique involves the use of powders and may be called direct powder rolling. In this technique, atomized iron powders and silicon powders are blended by ball milling and then subjected to rolling. This process merely shapes the powder compacts and re-agglomerates the powders into a thin strip. High-temperature annealing must be performed to alloy and homogenize the compacted strip. Li et al. produced 60-mm-wide and 0.2–0.35-mm-thick 6–6.5 wt% silicon steel strips by this method [125]. The annealed strip has a saturation induction value of 1.795 T, which is close to the theoretical value. However, the iron loss of the strip remains high. Although direct powder rolling effectively mitigates the brittleness issue, it brings in new problems such as contamination of powders, nonhomogeneous composition, and limitation in strip length.

2.5.2. Rapid solidification

The brittleness of high silicon steel originates from the B2 and D03 ordering. Rapid solidification techniques that surpass the ordered phases are thus widely studied for the production of high silicon steel.
One of the most widely used techniques in rapid solidification is melt spinning. In the melt spinning process, alloys are inductively melted in a crucible before being ejected onto a rotating wheel. Such a process directly produces continuous thin ductile strips with 10–100 µm thickness. A typical melt spinning setup is shown in Figure 2.11. Melt spinning was used by Arai and Tsuya to produce 3.8 to 9.3 wt% silicon steel ribbons as early as 1980 [72]. Recent efforts by Lin’s group [51, 126] has brought the melt spinning of 6.5 wt% silicon steel one step further toward the production of large-scale ribbons with 25 mm width and 0.03 mm thickness. The melt-spun thin ribbon is ductile and can be bent 180° without cracking [66]. The magnetization of melt spun 6.5 wt% silicon steel is around 1.78 T; however, its coercivity can be large due to the small grain size and large strain [50, 72]. Nevertheless, the coercivity may be reduced by high-temperature annealing, with 1200°C for 35 min as the most suitable condition to produce the lowest coercivity [72]. Due to the presence of heat gradient from the ribbon wheel side and free side, the grains tend to grow columnarly along the ribbon thickness direction resulting in a certain degree of a <100> out-of-plane fiber texture [50, 88]. This favorable texture makes melt-spun ribbons especially desirable for motor applications.

Many process parameters such as melt temperature, nozzle size, nozzle-to-wheel distance, wheel material, wheel speed, overheat, chamber gas, chamber pressure, and injection pressure must be closely controlled to obtain continuous high quality ribbons. Nickel-plated copper wheels were found to be the optimum wheel owing to their wetting behavior, whereas copper wheels could not produce well-shaped ribbons efficiently and steel wheel was found inefficient in cooling when processing large quantity of melt due to poor conduction [88]. Helium, compared to argon gas, created a less violent gas boundary layer, thus resulting in fewer air pockets and better ribbon shape [88]. Furthermore, the wheel speed affects the cooling rate and ribbon thickness [50], thereby can be used to control the degree of ordering [50], which in turn affects the mechanical properties and coercive force [50, 111]. Electrical resistivity, however, remained constant for different wheel speeds [111]. Adjusting the wheel speed offers an opportunity to tune the texture and grain size as well as the ordering. Figure 2.12 shows the difference in ordering at two different wheel speeds, and the <001> out-of-plane texture produced at a high wheel speed.

Melt spinning enables a direct production of ductile Fe-6.5wt%Si thin sheet and can save a large amount of energy by avoiding the energy-consuming rolling processes. The wheel usually
spins at 30 m/s, which implies a production speed of 30 meters of sheet per second. The rapid quenching also minimized the oxidation, which eliminated the need for an acid wash, thus minimizing impact to environment. However, at its current stage, melt spinning can only offer a limited range of thickness (0.03-0.1 mm) and width (<300 mm), and is now mainly used in laboratories to produce 6.5 wt% silicon steel in small scale (<1 kg/batch).

Figure 2.11. Schematic depicting a typical set up of a melt-spinning system.
As another rapid solidification technique, strip casting was explored for the processing of Fe-6.5wt%Si steel. In the strip casting process, superheated molten metal is poured into a preheated tundish, where it is then flowed down through a nozzle onto water-cooled steel or copper rolls. A 1 to 2 mm thick cast strip is then air cooled to room temperature. Strip casting offers a high solidification rate and can produce strips with thicknesses close to that of the hot-rolled sheets. Wang’s group recently conducted a series of studies on strip casting of silicon steel [89, 90, 127-134]. Strip casting of 3 wt% silicon steel was successful [89], and strip casting of 6.5 wt% high silicon steel was attempted [90, 127]. However, rolling of the strip cast sheet remains challenging due to the lack of sufficient ductility [90, 127]. The iron loss of 22–24 W/kg at 1 T and 400 Hz of the annealed strip [90, 127] is high. The preferred <001> out-of-plane fiber texture is observed on
the strip cast sample [89, 129]. The degree of the texture was found to be dependent on the superheat, with high superheat resulting in elimination of equiaxed grains and improvement of the <001> fiber texture [89]. The preferred orientation randomizes after the subsequent rolling process. To retain the <001> fiber texture, an additional 1200°C hot rolling process was found to be useful [90, 127].

Strip casting allows the production of continuous strips several millimeters in thickness, and eliminates the hot rolling and acid wash step involved in the production of steel laminates. When needed, warm and cold rolling may be added to the strip casting line with ease. However, production of strip-cast high silicon steel with the desired thickness and sufficient ductility remains a challenge.

Though a desirable texture can be generated via various processing techniques, the microstructure is likely to be randomized during subsequent high-temperature annealing which is essential to achieve good magnetic properties. One way of maintaining the preferred texture is by directional recrystallization, wherein the sample is passed through a hot zone with a temperature gradient to achieve directional recrystallization. This process favors the growth of columnar grains, thereby inducing a preferred orientation. Various reports on directional solidification/recrystallization are available in the literature [62, 91-93, 135, 136]. For example, \{110\}<111> and \{111\}<110> texture components were introduced to Fe-6.5wt%Si high silicon steel using a 1150°C directional recrystallization process [91]. The coercivity of the obtained sample in the direction 60° away from the growth direction is remarkable, reaching 13.9 A/m, which is the result of oriented grains and a large grain size. The processing parameters such as hot zone temperature [92], growth rate [92], and directional solidification rates, i.e., the specimen-withdrawing velocity [92] can be tuned to optimize the texture.

2.5.3. Deposition/diffusion annealing

The deposition/diffusion annealing approach utilizes ductile low silicon steel as feedstock. A higher silicon content is achieved through surface deposition techniques of high silicon containing chemicals. Diffusion annealing is then performed to achieve uniform distribution of silicon. The deposition method varies, including chemical vapor deposition (CVD), hot dipping, physical vapor deposition (PVD), and spray forming.
NKK Corporation, now a part of JFE steel, pioneered the production of gradient 6.5 wt% Si steel using CVD approach [35, 97, 137]. In their process, Si is deposited on the surface of 3 wt% Si steel sheet by passing silicon tetrachloride (SiCl\(_4\)) gas over and then allowing Si to diffuse into the bulk at 1200°C [138]. The following chemical reaction occurs during the diffusion process.

\[
\text{SiCl}_4 + 5\text{Fe} \rightarrow \text{Fe}_3\text{Si} + 2\text{FeCl}_2
\]  

Such a CVD process has some drawbacks such as the limitation of sheet thickness and high environmental impact due to the use of harmful SiCl\(_4\). The health effects upon exposure to SiCl\(_4\) have been mentioned in literature [139, 140] and media [141].

The hot dipping and diffusion annealing route to producing 6.5 wt% gradient silicon steel was introduced by Ros-Yanez et al. [118, 142]. In this method, 0.35-mm-thick 3.2 wt% silicon steel was dipped into an Al-Si hypereutectic bath (25 wt% Si) at 800°C to achieve a multilayer Fe-containing intermetallics, which was then annealed at 1250°C for 30 min to achieve homogeneous Si and Al concentrations of up to 6.5 wt% and 4.5 wt%, respectively. The sample immersed for 100 s and annealed at 800°C for 60 s showed a power loss of 33.57 W/kg at 1 T and 400 Hz; further annealing at 1250°C for 30 min resulted in W10/400 of 10.56 W/kg. This method is similar to the JFE steel CVD process and may have potential for mass production. However, the introduction of aluminum is unavoidable, which may adversely affect the magnetic properties such as magnetization and magnetostriction.

PVD methods have been investigated such as electron beam PVD [143] or magnetron sputtering deposition. However, the formation of pores [143] or porous interfaces [144] remains a problem and adversely affects the magnetic properties [143]. While the application of PVD method may be viable for small samples, the mass production of wide sheet is challenging.

Spray forming uses a carrier gas such as Ar to spray atomize liquid metal Si onto a rotating iron substrate [123] or strip [145]. Then, the samples are homogenized at 1100°C for 10 h [123] followed by rolling to reduce the strip to thinner gauges. To increase the ductility during the rolling process, Al was added to the cold spraying process [146-148], which improved the ductility due to the avoidance of B2 ordering owing to the presence of Al; however, the formation of inclusions impaired the magnetic properties. A recent effort by Cava et al. [149-151] focused on co-spraying
Fe-3.5wt%Si + 3 wt% Si on a 1020 steel substrate. However, the presence of oxide particles in the final microstructure remains a problem.

2.5.4. Comparison of magnetic properties

The magnetic properties of 6.5 wt% silicon steel is plotted in Figure 13 [35, 47, 80, 90, 97, 120, 122, 126, 127, 142, 144]. The iron losses are dependent on the thickness, except at a low frequency of 50 Hz. The low frequency loss W10/50 has a significant contribution from the hysteresis loss, and thus, the thickness dependence is not prominent, and the typical losses range from 0.5 W/kg to 0.7 w/kg for all the methods referenced. Eddy current loss makes a larger contribution when testing at higher frequency. The dependence on thickness at high frequencies is thus more significant, with thinner thicknesses generating much lower iron losses.

Figure 2.13. Comparison of AC magnetic iron losses of Fe-6.5wt%Si steel produced by different methods tested at different conditions [35, 47, 80, 90, 97, 120, 122, 126, 127, 142, 144]
2.6. Application

Soft magnetic materials are extensively used in the fields of electricity conversion, electric machines, sensors, EMI prevention, and electronic components. This section provides a brief introduction of the potential applications of high silicon steel and the desired materials properties.

2.6.1. Electricity conversion

Electricity are frequently converted between AC and DC, and between different voltages and frequencies. Devices such as transformers, inverters, converters, and frequency modulators accomplish the conversion using soft magnetic materials [152]. Transformers are used to alter the AC voltages. Based on the operating frequency, the transformers can be classified as 50/60 Hz distribution transformers [153, 154], 400 Hz transformers [25], and high-frequency (audio/radio) transformers [31, 40]. While 50/60 Hz transformers are extensively used in residential applications, 400 Hz transformers are popular in aviation industry [155] and military applications [156] where high power density is desired. Inverters convert DC power to AC power, and are primarily used by solar power systems, fuel cell power systems, uninterruptible power supplies [157], and electric vehicle motor drives [156, 158]. Converters are used to convert AC to DC for battery charging, and frequency modulators which modifies frequency.

For applications in the frequency range of $0-10^2$ Hz, cost is the primary consideration. While high saturation magnetization and high permeability are highly desired, high electrical resistivity ($>50 \, \mu\Omega\text{-cm}$) is also preferred but not as critical. In addition, low coercivity and low hysteresis are required for a low power loss. In contrast, for applications in the frequency range of $10^2-10^{10}$ Hz, high electrical resistivity is necessary. The requirements also include high permeability and low power loss [159]. High silicon steel (6.5 wt% Si) satisfies all the requirements for low to medium frequency applications (up to 1 kHz) and has become a candidate for applications in high-frequency (up to 15 kHz [160]) inductors in the automotive, aerospace, and stationary power generation industries [161]. Currently, 6.5 wt% silicon steel from JFE steel prepared by the CVD process are used as the core materials of the inductors of 15 kHz buck-boost converters in Toyota Prius hybrid electric vehicles (HEVs) [160]. Other 6.5 wt% silicon steel products such as MEGA flux from Chang Sung Corporation [162], XFLUX from Magnetics Inc. [163], Fluxsan from Micrometals Inc. [164], and DF series from Hengdian Group [165] are also
commercially available for inductor applications [166]. The performances of Fe-6.5wt%Si powder core, ferrite core, and nanocrystalline core for the inductor of a buck-boost converter were compared by You et al. [160]. And Fe-6.5wt%Si powder core was found favorable owing to its high saturation, low core losses at 10 KHz, high thermal stability, low acoustic noise, and more importantly, low cost [160].

2.6.2. Electric machine

Electric machine has two variations, one is power generator and the other is electric motor. The rotating magnetic field between a rotor and a stator leads to the conversion of mechanical energy into electrical energy for generators and the reverse conversion for motors. The application of advanced soft magnetic materials to rotors and stators is the key for high efficiency motors which operates at high frequencies to meet the trend of system miniaturization and cost reduction [101, 167-170]. For electric machines to achieve their best performance, high magnetization, high permeability, low coercivity, high electrical resistivity, and high Curie temperatures are indispensable magnetic properties [171].

Non-oriented silicon steel finds many applications in electric vehicle. Its application includes traction motors, power steering motor, wind-shield wiper motor, seat adjuster motor, fuel pump, HVAC compressor and fans, window life motor, and electrical turbocharger motors. The 6.5 wt% Si steel is more attractive due to its low raw material cost, near-zero magnetostriction, and low iron losses at higher frequencies [101].

2.6.3. Sensors

Sensors convert energy from one form into another to detect, measure, and analyze the source signal. The demand for high-performance and cost-effective sensors is rapidly growing [172]. Various magnetic effects are employed by sensors, such as electromagnetic effect, Hall effect, magnetoresistive effect, magnetoelastic effect, and giant magnetoimpedance effect [173]. These effects are used in a number of devices such as magnetic field sensors [174], stress/strain sensors [172, 175, 176], current sensors [177], temperature sensors [178, 179], and light sensors [180]. In general, a sensor material should have low coercivity, temperature-stable permeability,
and high electrical resistivity [181]. However, individual sensors may have different requirements due to the nature of the magnetic effects being utilized.

Magnetic sensors are widely used in the automotive industries such as anti-lock brake system sensor rings, pump angle sensors, ignition system pulse generators and rotational speed sensors, power steering system rotation and torque sensors, and electronic gearbox control system input and output speed sensors. [182]. Currently, these sensors use ferrite, stainless steel, or iron. However, these can all be the potential applications of the 6.5 wt% silicon steel, which is capable of delivering lower losses. Particularly, the 6.5 wt% silicon steels may be a direct replacement for silicon steels in which are used in high-frequency pulsed current step motor sensors, where these sensors are used to provide electronic control of the valve openings [182].

2.6.4. Electromagnetic interference (EMI) prevention

EMI is the electromagnetic disturbance that degrades the performance of electrical circuits [183]. With the ever-increasing utilization of electronic devices in our daily lives, EMI prevention have been attracting great interests for devices protection. One form of protection is the common mode chokes, which operate by acting as a low-impedance wire to pass the desired signal and as a high-impedance inductor to block high-frequency noise [184]. Electromagnetic field shielding prevents EMI as well [185, 186]. It could be used either for passive shielding by drawing the magnetic field into itself, or for active shielding by generating a field to eliminate the external field. These applications largely pertain to the aviation and telecommunication industries [187].

The materials used for EMI applications require a high initial permeability and remain stable in frequencies up to 10 MHz, and should maintain high impedance within a wide frequency range and at high operating temperatures [188]. The currently popular EMI materials are Ferrites [189], amorphous, nanocrystalline alloys, and iron-nickel alloys [190]. However, with the increasing demands for higher flux densities [191], materials with high magnetic saturation and high electrical resistivity would be necessary. High silicon steel could be a viable candidate if its electrical resistivity is further enhanced by forming a composite with non-conductive coating materials.
2.6.5. Electronic components

Soft magnetic materials are widely employed in electronic components. Among them, applications in the fields of data storage and telecommunication are of tremendous significance in the current information age. The magnetic read/write head material for data storage is a good representation in this field [192, 193]. These materials must have high magnetization, high initial permeability, high mechanical hardness, high wear resistance, and near-zero magnetostriction [31]. Telecommunication applications deal with transmitting information via the conversion between electric current and electromagnetic wave [171], which requires a low core loss at a high frequency (MHz to GHz) [194]. Additionally, numerous electronic components take advantage of soft magnetic materials to perform their functions, such as circulators, isolators, limiters, phase shifters [184], pulse transformers [195], inductors [196, 197], switches [198], and amplifiers [185]. Examples of soft magnetic materials in this category may include dimmer switches, contact plates, heater valves, relay armatures, and gas security valve cores [182]. For parts that require high resistivity and high permeability, silicon steel is the usual choice, such as printer heads in the impact printers used in automated teller machines [182].

2.6.6. Others

In addition to magnetic properties, soft magnetic materials demonstrate other advantageous properties. For instance, a low Young’s modulus allows soft magnetic materials to be used as automobile valve springs [195]. Similarly, high stiffness is the optimal property for the materials of certain sporting goods, such as golf clubs, baseball bats, snowboards, and fishing equipment [199]. Soft magnetic materials are extensively utilized in chemical and medical applications as well [200, 201].

2.7. Summary

Soft magnetic materials find wide applications in today’s electric and electronic world. While soft magnetic materials enables energy conversion, they consumes a significant amount of energy during the process due to the iron loss. To conserve energy and meet the increasing demand for high-frequency operation, the iron loss of soft magnetic materials needs to be minimized. High silicon steel, more specifically, 6.5 wt% silicon steel possesses high electrical resistivity, high
saturation magnetization, zero magnetostriction, and low raw material cost, which make it a promising candidate for mid-frequency applications. However, 6.5 wt% silicon steel is brittle due to the formation of ordered phases, and cannot be processed using the economical cold rolling method. A number of processing techniques such as thermal mechanical processing, rapid solidification, and deposition/diffusion annealing have been investigated for manufacturing ductile 6.5 wt% silicon steel sheet. These methods have drawbacks including high cost, limitations in width and thickness, and adverse environmental impact. To enable the wide application of 6.5 wt% silicon steel, these drawbacks, in particular, the overall processing cost must be thoroughly addressed.

Fe-6.5wt%Si steel can be used in various forms such as wound tape, stacked laminates, or powders/flakes compacts. It is important to obtain ductile Fe-6.5wt%Si sheet by suppressing the embrittling ordering phases, as ductility is needed for the subsequent mechanical processes such as spooling or stamping. The ability to prepare sufficiently wide sheet is critical, as it is the basis for large laminates for electric motors. It should be noted that the ultimate goal is to achieve the optimum magnetic property with the material in its final form. In most cases, the rapidly solidified disordered Fe-6.5wt%Si steel with fine-grains cannot be directly used because the ordered B2 and D0₃ phases that are responsible for better magnetic properties are missing [63]. Annealing is required to call back these phases, relieve stress and increase grain size, albeit additional annealing process inevitably imposes processing complexity.
CHAPTER 3 EFFECT OF WHEEL SPEED ON MAGNETIC AND MECHANICAL PROPERTIES OF MELT SPUN FE-6.5WT%SI HIGH SILICON STEEL

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Abstract

Fe-Si electric steel is the most widely used soft magnetic materials in electric machines and transformers. The superior magnetic and electric properties of 6.5 wt.% high silicon steel may improve efficiency and power density of electric machines. However, the brittleness due to the formation of B2 and D03 ordered phases in high silicon steel makes it difficult for large scale application. It is known that these ordered phases can be fully or partially suppressed by rapid cooling. However, further study is needed to understand the extend of cooling on the magnetic and mechanical properties of 6.5 wt.% silicon steel with various degree of ordering. By tuning the wheel speed from 1m/s to 30m/s of the melt spinning process, varying degrees of cooling were achieved on 6.5 wt.% silicon steel ribbons. The cooling rate significantly altered the ordering, microstructure size scale, and thus the mechanical and magnetic properties. X-ray showed that D03 ordering can be fully suppressed at high wheel speed, but started to nucleate at 10m/s and below, which correlates with the Young’s modulus increase towards low wheel speeds as tested by nano indentation. The grain sizes of the ribbons on the wheel side decreased with increasing wheel speeds, being ~100 µm at 1m/s and ~8 µm at 30m/s, which led to the change in coercivity. Saturation magnetization of the ribbons remained about 1.74T to 1.78T, which appeared to be mainly depend on the chemistry.

3.1. Introduction

With increasing demand on higher energy efficiency on motors, generators and transformers, new generation of soft magnetic materials is needed. Ever since Gumlich[202] discovered the favorable effect of silicon to iron in soft magnetic properties more than 100 years
ago, Fe-Si has been the ideal choice of such applications. Currently, up to 3.2 wt.% silicon steels are used predominately in the market and it is called low silicon steel. They are cold rolled to thin sheet with ease, then laminated for usage. Silicon content higher than 3.2 wt.% is called high silicon steel. High silicon steel faces challenge in processing, but its higher resistivity is very attractive. The electric resistivity increases from 48 \( \mu\Omega\text{-cm} \) to 82 \( \mu\Omega\text{-cm} \) when silicon content is increased from 3 wt.% to 6.5 wt.%, resulting in much lower energy losses for 6.5 wt.% silicon steel [203]. 6.5 wt.% silicon steel also offers other unique properties, including low magnetocrystalline anisotropy and zero magnetostriction [34], leading to higher permeability and lower operation noise.

Fe-Si electric steel present as substitutional A2 body centered cube (bcc) structure at low silicon concentration. When silicon concentration is increased to about 5.3 wt.%, B2 ordering starts to appear below 500°C according to the phase diagram [59, 204]. DO3 ordering starts to appear when silicon content is further increased beyond 6 wt.%. A2 is in the dis-ordered state, where the distribution of Fe and Si is random. B2 and DO3 resulted from ordering of nearest neighbor and next-nearest-neighbor atoms. Unlike-atom paring of the nearest neighbor atoms results in B2 ordering and further ordering between the next-nearest-neighbor atoms results in DO3 ordering [59]. The ordering interacts with dislocations resulting in a strengthening effect [61], which adversely affects the mechanical properties. Superdislocation slip deformation mechanism as proposed in B2 and DO3 lattice [62] also deteriorates the mechanical properties.

A majority of research in the field of high silicon steel focuses on solving this brittleness problem while maintain and enhance its magnetic properties. A few techniques have enabled the processing of high silicon steel including thermal mechanical processing (hot roll and cold rolling) [115, 120, 122], rapid solidification [88, 205-207] and deposition/diffusion annealing [35, 137, 144]. These methods utilize disordered A2 state during processing either by usage of high temperature or rapid solidification. Cooling rate of the rapid solidification process plays significant effect on the ordering and thus the physical properties of high silicon steel produced. However, the effect of cooling rate is not thoroughly studied yet. In this study, 6.5wt.%Si silicon was produced using various wheel speed in the melt spinning process. The effect of wheel speed on the ordering and physical properties of the melt-spun ribbons was systematically studied.
3.2. Experiment

Fe-6.5wt.%Si ingots were prepared by arc melting in Ar atmosphere. Charge of 6g each were loaded into 18mm diameter quartz tube, then inductively melted to 1590°C prior to ejecting through an orifice of 0.8mm in diameter with 120 Torr He over-pressure onto a single rotating copper wheel. The copper wheel was 2.5cm wide and 25cm in diameter. The chamber was partially filled with He to 250 Torr pressure. Melt-spinning was performed at seven different wheel speeds: 1m/s, 3m/s, 5m/s, 7m/s, 10m/s, 20m/s and 30m/s, where the speed was controlled by an external DC motor with digital control using ferro-fluidic coupling.

To characterize the degree of order, transmission X-ray diffraction (XRD) was performed on the ribbons using single crystal x-ray diffractometer (STOE IPDS, STOE & Cie GmbH) with Mo source. The incident beam and the image plate detector was fixed, while the sample rotated from 0° to 180° ω angles to acquire the ring patterns. The ring patterns were later integrated to generate the θ-2θ XRD pattern for evaluation of relative intensities. The grain sizes were measured on the wheel side of the ribbon using backscattered imaging model in Scanning Electron Microscopy (SEM) (Teneo, Fei Inc). The magnetic properties of the ribbons were measured using Vibrating Sample Magnetometer (VSM) (Versalab, Quantum Design, Inc.). Five falkes with the dimension of roughly 1mmX4mm were used for each speed. The coercive force was measured with a maximum field of 8000A/m, while the saturation magnetization was measured up to 1 Tesla. The mechanical properties of the ribbons were characterized using nano-indentation (NanoTest™, Micro Materials Ltd) technique. The ribbons were mounted sideways in the epoxy mounts. The ribbon cross-sections were then polished to a final finish using 0.05 colloidal silica for nano indentation tests. Depth versus load method was used with fixed loading rate of 5.0 mN/s and maximum load of 50 mN. 10 indents were made by 3-faceted Berkovich diamond indenter on each sample in the middle of the cross-section with spacing of 30 micron.

3.3. Results and discussion

Various degree of ordering was resulted at different wheel speed as shown in Figure 3.1. Inside the fundamental (110) rings, additional superlattice ring belonging to D03 ordering can be clearly seen on low wheel speed samples. This D03 superlattice ring was missing in 20m/s and 30m/s samples. For all the wheel speed experimented, D03 ordering starts to appear when wheel speed is below 10m/s, and becomes apparent below 5m/s. Integration and normalization of rings
allows relative intensity to be calculated. The increase in D03 relative intensity (Sample \( \frac{I_s}{I_f} \)) towards low wheel speed is clearly seen in Table 3.1. Quantification of B2 using its superlattice (200) peak at around 14° is difficult due to its overlapping of D03 peak and low relative intensity (53% of that of the D03 (111) peak at ~10°).

![Figure 3.1. Two-dimensional X-ray diffraction patterns of various wheel speed.](image)

Long range order parameter (LROP) has been used to quantify the relative amount of superlattice peak [18]. LROP can be calculated using the following equation:

\[
LROP = \left( \frac{I^s}{I^f} \right)^{1/2} \quad (1)
\]

where \( I^s \) and \( I^f \) are the relative intensity of the superlattice peak and the relative intensity of the fundamental peak of the sample, while \( I^s_0 \) and \( I^f_0 \) are the relative intensity of the superlattice peak and the fundamental peak of the ordered D03 from the reference according to Pearson crystal database. (111) peak and (110) peak were used for the superlattice peak and the fundamental peak respectively. As can be seen in table 1, LROP increases with increasing wheel speeds, representing a higher degree of order in samples melt-spun at lower wheel speeds. The reason why LROP is greater than unity is like due to the higher intensity of low angle peaks in transmission mode.
It is known that the wheel speed alters the surface cooling rate [209]. The cooling rate of a similar alloy system (Fe (75 at.%), Si (10 at.% and B (15 at.%)) using the same instrument varied from 1.5X10⁵ to 1.42X10⁷ at 5m/s and 20m/s wheel speed respectively [209]. It is generally accepted that faster cooling rate can be achieved on higher wheel speed experiment where the heat can be removed more rapidly. The average cooling rate experienced by the ribbon can be expressed by the following equation [210]:

\[
\frac{dT}{dt} = h \frac{\left(T_i - T_w\right)}{\rho x c_p} \quad (2)
\]

where \(h\) is the heat transfer coefficient, \(T_i\) is the initial temperature of the ribbon and \(T_w\) is the temperature of the wheel, \(x, \rho\) and \(c_p\) are the thickness, density and heat capacity of the ribbon formed respectively.

For a given material, the cooling rate is controlled by \(x\) and \(h\). \(x\) is dependent on the wheel speed \(v\) by volumetric flow rate of the melt from the nozzle (Q) according to [210]

\[
\frac{x^2 v}{Q^{1/2}} = constant \quad (3)
\]

Therefore, a direct relationship can be drawn between wheel speed and cooling rate. The difference in degree of order observed is a result of different cooling rate achieved.

Table 3.1. Relative intensities (with background subtracted) of superlattice peak (111) versus fundamental peak (110) and long range order parameter with change in wheel speed.

<table>
<thead>
<tr>
<th>Wheel speed (m/s)</th>
<th>Sample ((I_s/I_f))</th>
<th>D03 ref ((I_0^S/I_0^F))</th>
<th>LROP</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.054</td>
<td>0.06</td>
<td>0.94</td>
</tr>
<tr>
<td>3</td>
<td>0.012</td>
<td>0.06</td>
<td>0.45</td>
</tr>
<tr>
<td>5</td>
<td>0.065</td>
<td>0.06</td>
<td>1.04</td>
</tr>
<tr>
<td>7</td>
<td>0.007</td>
<td>0.06</td>
<td>0.34</td>
</tr>
<tr>
<td>10</td>
<td>0.002</td>
<td>0.06</td>
<td>0.17</td>
</tr>
<tr>
<td>20</td>
<td>0.002</td>
<td>0.06</td>
<td>0.18</td>
</tr>
<tr>
<td>30</td>
<td>0.002</td>
<td>0.06</td>
<td>0.20</td>
</tr>
</tbody>
</table>
The grain size on the wheel side of the ribbon as a function of wheel speed is plotted in figure 2. Increase in the grain size was observed when wheel speed was decreased. The grain refinement on rapid solidified alloys was discussed in detail by Greer [211]. The microstructure of melt spun ribbon is characterized by a fine equiaxed chill zone at the wheel side where columnar grain grows. The initial grain size of the ribbon at the wheel side is dependent on crystal growth rate, heterogeneous nucleation frequency and the time for solidification of the surface [211]. With substantial initial undercooling available in the melt-spun ribbon, a simply equation was given [210], which says grain size is inversely proportional to the wheel speed $V$ and the cooling rate $\frac{dT}{dt}$. Good linearity was observed when the grain size was plotted against inverse of wheel speed with R-squared value of 0.97 as shown in the insert of figure 3.2. The increase in grain size with decrease in wheel speed is also reflected in the X-ray diffraction rings in figure 1, where the fundamental rings, for example (110) rings, changing from continuous to discrete due to fewer grains lying in the x-ray beam path for samples with larger grains.

![Figure 3.2](image)

Figure 3.2. Grain size as a function of wheel speeds. Insert shows the grain size plotted as a function of inverse of wheel speeds.
Based on the loading and unloading curves from the nano indentation experiment, power law fit pyramidal analysis were made. Important parameters such as reduced modules and hardness were thus calculated based on the analysis. Young’s modulus was calculated using the following equation referencing to Oliver and Pharr[212].

\[
\frac{1}{E_r} = \frac{1-\nu_s^2}{E_s} + \frac{1-\nu_i^2}{E_i}
\]  

(4)

where \(\nu_s\) = Poisson's ratio for the sample (0.3 in the case of silicon steel), \(\nu_i\) = Poisson's ratio for the indenter (0.07), \(E_r\) = Reduced modulus of the sample, \(E_s\) = Young's modulus for the sample and \(E_i\) = Young's modulus for the indenter (1141 GPa). Young’s modulus as a function of wheel speed was plotted in figure 3. A clear trend can be seen that Young’s modulus reduces with increasing wheel speed. This effect is more prominent when the speed was increased from 10m/s to 20m/s, while fluctuating up and down below the 10m/s range. It is known that ordering of Fe-Si results in brittleness and fast quenching is capable of producing ductile ribbons bypassing the disorder to order transition. The reduction in Young’s modulus allowed us to quantify the ductility of the quenched alloy. Nano indentations was also applied to sample annealed at 850°C followed by slow cooling. Young’s modulus of 177.78 GPa and hardness of 5.90 GPa was measured. Due to the higher ordered phase concentration in annealed sample, its higher modulus and hardness was expected. Similar trend was observed in the hardness plot in figure 3, with 1m/s as an exception. In the hardness measurement, the standard deviation for each sample was high, probably due to its high sensitivity to microstructure effect.
Figure 3.3. Young’s modulus and hardness as a function of wheel speed as measured by nano-indentation. Young’s modulus is plotted to the axis on the left, hardness was plotted to the axis on the right. The horizontal axis of hardness was slightly shifted right for better visualization.

The magnetic properties of the melt-spun ribbons are shown in figure 3.4. The saturation magnetization of the ribbons witness no big change. They stayed between 1.74T to 1.78T at 1T maximum field level. It is likely that the saturation magnetization depends primarily on chemistry of the alloy. With the Si level remained around 6.5 wt.% by EDS studies, no change in saturation magnetization is to be expected. High wheel speed samples displayed steeper square loops than the ones of lower wheel speeds indicating higher permeability. The change in permeability is likely due to the varying degree of texture present in the samples. \(<100>\) being the easy magnetization axis for body centered cubic crystals, higher permeability is a result of higher degree of \(<100>\) texture. \(<100>\) out of plane fiber texture was observed on 30m/s using XRD pole figure technique, which was resulted from the columnar grain growth along the heat extraction direction away from the wheel. The relative intensity of \(\{200\}\) planes was found to decrease with decreasing wheel speed when surface XRD was scanned on the sample free side, suggesting a decrease in out of plane \(<100>\) texture. Wheel speed resulted in a considerable change in the coercive force of the ribbons. The coercive forces are 110.8 A/m, 99.8 A/m, 60.5 A/m, 47.5 A/m, 33 A/m, 32.5 A/m,
30.0 A/m for wheel speed of 30m/s, 20m/s, 10m/s, 7m/s, 5m/s, 3m/s, 1m/s respectively. The decrease in coercive force match well with the increasing in grain size as shown in figure 4 with decreasing wheel speed, where grain size plays a dominant role in coercive force.

Figure 3.4. Magnetic properties M-H plot of the ribbons with various speed. Insert shows the MvsH near origin for clear vizualize of the coercive force.

3.4. Conclusion

By altering the wheel speed of the melt spinning process, various degree of cooling has been achieved. The difference in cooling rate has brought about changes in degree of ordering and grain size. Faster wheel speed results in lower degree of order and smaller grain size. D03 ordering started to appear at wheel speed 10m/s, while it disappeared for wheel speed 20m/s and 30m/s. Grains with average size of 8 µm was present on the 30m/s spun ribbons while it quickly coarsened when the wheel speed was lowered, reaching 132 µm on the 1m/s spun ribbons. The change in degree of order and grain size significantly affects the mechanical and magnetic properties including Young’s modulus and coercivity. For improved ductility of the ribbon, it is suggested that the wheel speed to be 20m/s and above.
CHAPTER 4 EFFECTS OF WHEEL SPEED ON THE MATERIAL PROPERTIES OF FE-6.5WT%SI

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Abstract
The change in electrical resistivity, magnetic saturation, and micro hardness of melt-spun ribbons at various wheel speeds was investigated in an attempt to correlate with the formation of ordered phases. The material properties of melt-spun ribbon processed at different wheel speeds are studied for clear shifts, which, if present could indicate the presence of A2, B2 and D03 in the crystal structure. Since the A2 phase is a metastable phase at room temperature there should be a critical wheel speed at which the transition is clearly defined and lead to a qualitative test that can be performed in the future to confirm the final microstructure.

4.1. Introduction
The effect of wheel speed on properties of melt-spun Fe-6.5wt%Si has been explored on a number of mechanical, magnetic, and structural properties in Chapter 3. While these tests provided a first pass at the processing-properties relationship present in the system there are more tests that can be done. This paper seeks to identify the relationship between wheel speed and electrical resistivity, magnetics saturation, and micro hardness in melt-spun ribbons. The methods that will be explored are four-point wire resistivity measurements, vibrating sample magnetometer, and Vickers micro hardness. Each method will test multiple ribbons at various wheel speeds looking for trends that indicate the presence of B2 and D03 in the sample. These tests will then be compared to literature values for each pure structure in an attempt to either qualitatively or quantitatively identify their presence.

4.2. Methods
Melt-spun ribbons were produced at wheels speeds of 30, 20, 10, 7, 5, 3, 1 m/s using the procedure described in Chapter 3.2. Long fully intact ribbons were achieved with each wheel speed
above 7 m/s, while at lower speeds the ribbon length became drastically shorter. Each set of ribbons was then cut to length and prepared for each individual test.

The first experiment conducted was examining the electrical properties of the melt-spun ribbon. Samples were cut into 10 mm long segments from the straightest sections of the ribbons as shown in Figure 4.1. Due to the surface texture and ribbon instability samples below 7 m/s were unable to be measured with this method as no single piece of ribbon could meet the sample length requirements. Afterward each sample was placed onto an insulated pad and four gold wires were laid across at four points with nearly equal spacing. Another insulating pad was then applied on top along with 100 gram weight to apply even pressure across the wires. A current of varying strength was then applied to the ribbons and the corresponding voltage drop between the center two wires was collected. The current was then applied in reverse and the voltage drop again was recorded. The average of these two voltages yields the correct voltage for an applied current. Afterward the voltages were plotted and the slope of their line recorded.

The second experiment consisted of cutting the melt-spun ribbon into segments of approximately 4 mm long and stacking them together using a varnish. Once a stack of ribbons was approximately 4mm x 4mm x 4mm it was then loaded onto a CuBe sample holder as shown in Figure 4.2 and placed inside the VSM. The samples were then magnetized to 3 Tesla back to no field and then -3 Tesla then back again to no field. The average of the two magnetic saturations was then collected.

The final experiment consisted of using a Vickers hardness indenter to measure the hardness of the material. Ribbons were mounted on edge in Bakelite and polished to a flat surface. Once loaded into the machine a
load of 100 N was applied for 5 seconds and 10 measurements were taken per sample. Each wheel speed had 3 samples tested. The measurements were taken from the center of the ribbon edge as to avoid any edge effects from the polymer matrix holding the ribbons as is shown in Figure 4.3.

4.3. Results

The voltages and currents from the first experiments were then used to calculate resistivity of material using the following equation.

\[
\rho = R \left( \frac{A}{s} \right) = R \left( \frac{w \cdot t}{s} \right) = \left( \frac{V}{I} \right) \cdot \left( \frac{w \cdot t}{s} \right)
\]

Where V is voltage, I is current applied, w is the width of the sample, t is the sample thickness, and s is the spacing between the middle two wires. The results were then averaged between multiple samples and are shown in Figure 4.4. The MS for each wheel speed was collected and averaged among multiple samples and is shown in Figure 4.5. The hardness data for each ribbon was averaged and plotted against the wheel speeds and can be seen in Figure 4.6.

4.4. Discussion

The electrical resistivity of the ribbons prepared at different wheel speeds shows a slight trend. While very slight and certainly

![Resistivity VS Wheel Speed](image1)

Figure 4.4: Resistivity results from the 4-wire probe measurement.

![Vikers Hardness](image2)

Figure 4.5: Vickers hardness of melt-spun Fe-6.5wt%Si.

![Saturation Magnetization of Melt-Spun Ribbon](image3)

Figure 4.6: Magnetic Saturation of Fe-6.5wt%Si ribbons.
complicated by the standard deviation, there appears to be an increase in the resistivity at lower wheel speeds. This may be due to the increased ordering seen in the B2 and D03 phases, however, without a shaper transition between wheel speeds it would only possibly serve as a qualitative signal that the ordered phases are present. It also points to the likelihood that electrical resistivity is relatively independent of atomic ordering and is more sensitive to the chemistry of the ribbons.

The Ms of the ribbons exhibited a slight trend of decreasing Ms with increasing wheel speed with 10 m/s as exception. Since magnetic saturation is determined by the arrangement of atoms with magnetic moment in the crystal lattice it is possible that as the system becomes more disordered at higher wheel speeds the silicon atoms begin to interfere with the preferred arrangement of iron atoms for maximum strength. This leads to the conclusion that while magnetic strength is often determined by the species present in an alloy the arrangement of those atoms can contribute to a reduction in Ms if disturbed. This at least leads to a qualitative method of determining if the crystal structure tends to a more ordered or disordered state in the melt spun ribbons. It is not clear the cause of the abnormally large magnetization of the ribbon prepared at 10 m/s.

The micro hardness experiment resulted in a clear indication of a brittle-ductile transition between 7m/s and 10m/s. This is the sign that a critical amount of ordering has taken place and either the B2 or D03 phases are present in the lower wheel speeds while they are suppressed at the higher wheel speeds. In addition there is another trend within the higher and lower wheel speeds themselves indicating that even once the threshold for ductile or brittle phases to form has passed further deviation results in an either harder for slower wheel speed or softer for higher wheel speeds. Additionally, when the 30 m/s sample was annealed its hardness returned to that of the lower wheel speeds, again suggesting the presence of the brittle phases B2 and D03.
CHAPTER 5 THERMODYNAMIC AND KINETIC ANALYSIS OF MELT SPINNING PROCESS OF FE-6.5WT%SI ALLOY

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Abstract

The microstructural evolution of Fe-6.5 wt.% Si alloy during melt spinning was studied. The solidification and solid-state diffusional transformation processes during rapid cooling were analyzed via thermodynamic and kinetic calculations. The Allen-Cahn theory was adapted to model the evolution of the bcc_B2 antiphase domain sizes for different cooling rates. The model was calibrated based on the experimentally determined antiphase domain sizes of the bcc_B2 phase for different spinning rates and the related cooling rates. Good correspondence of the theoretical and experimental data was obtained at high cooling rate up to 10⁶ K/s. Along with the asymptotic domain size value at the infinite cooling rates, the developed model represents a reliable extrapolation for the cooling rate > 10⁶ K/s and allow one to optimize the quenching process.

5.1. Introduction

It is known that Fe-6.5 wt.% Si alloy has optimum electrical and magnetic properties ideally suited for low-mid frequency electricity conversation. Compared to the commonly used 3.2 wt.% Si steel, saturation magnetization decreases by 10% (to 1.7 T) but permeability improves by 27% (to 19,000 at 1 kHz), while electric resistivity improves by 44% (to 82 μΩ-cm) and magnetostriction reduces from 7.8 ppm to 0.1 ppm (a transformer made of 6.5 wt.% Si steel will
be silent). However, Fe-6.5 wt.% Si is brittle. The presence of bcc_B2 and/or bcc_D0₃ ordered phases is responsible for the materials embrittlement [115]. Due to the low workability, high Si electrical steel sheet can not be manufactured by the conventional hot roll followed by cold roll method. Efforts have been made to mitigate the brittleness issue. Among them, the most commercially successful approach is to diffuse Si into the thin gauge 3.2 wt.% Si steel after chemical deposition. It was developed in the early 1990s by NKK Steel in Japan. Alternative manufacture methods, preferably using more conventional means, are being intensively pursued worldwide. Hot rolling has been demonstrated to produce thin gauge 6.5 wt.% Si steel sheet because the bcc_B2 phase can be avoided at temperature > 1123 K. Rapid quenching can temporarily suppress the heterogeneous formation of bcc_B2 and bcc_D0₃ phases [68]. The delayed formation of Si rich phases even allows a small processing window to perform the traditional cold-roll process. Melt spinning was used to produce 3.8 to 9.3 wt.% silicon steel ribbons by Arai and Tsuya as early as 1980 [72] and by Lin’s group in 2015 [51, 126]. The melt-spun thin ribbon can be ductile, as it may be bended 180° without crack [213]. And more recently, the effect of the melt-spin wheel speeds on physical properties of the obtained ribbon was experimentally investitaged by Cui’s group [50].

To date, there is no quantative study of the effect of cooling rate on ordering phase transition in Fe-6.5 wt.% Si alloy and corresponding modeling. Melt spinning technique can provide cooling rate up to 10⁵-10⁷ K/s [214] which is sufficient to systematically study the phase transitions during rapid cooling of high Si electrical steel. The present work aims to study the phase transitions during melt spinning of Fe-6.5 wt.% Si alloy by coupling experiments, CALPHAD calculations, and Allen-Cahn macroscopic theory of domain growth.

5.2. Experiments

Fe-6.5 wt.% Si alloy arc-melted in an argon atomsphere was utilized as raw materials for the melt spinning experiments. Quartz melt spin tubes was fitted with a 0.81 mm precision orifice. 6 g of raw material was inductively melted in the quartz melt spin tubes at 1863 K in the vacuum chamber partially filed with 1/3 of ultra purity helium. The melt was ejected onto a rotating copper wheel (2.5 cm in width and 25 cm in diameter) under a helium over-pressure of 120 Torr. Melt
spinning experiments were carried out at 3 m/s, 5 m/s, 7 m/s, 10 m/s, 20 m/s, and 30 m/s rotation speeds.

The process was monitored using a number of digital camera systems. FLIR A8303sc thermal camera with a N\textsubscript{2} filter was used to capture the temperatures of the ribbons surfaces during the melt spun process through a sapphire window. The thermal camera captures the temperatures of the ribbons in the temperature range of 773 K to 1573 K with a resolution of 1920×1080 and a pixel size of 0.7 mm. Thermal profile of the ribbon was obtained selecting two points along the ribbon and sampling the temperature along the line between them, which was then averaged using multiple frames and converted to temporal temperature profile, i.e. cooling rate, based on the actual distance per pixel and the wheel speed.

The as-spun ribbons were analyzed using transmission electron microscopy (TEM). The specimens were prepared using a FEI Helios NanoLab Dual-beam focused ion beam (FIB) with EasyLift micromanipulator and MultiChem Gas Injection System (MCGIS). The lamellae were lifted out from the wheel side of the ribbons and thinned using Ga ion beam. The samples were observed using a FEI Tecnai G2-F20 TEM equipped with a field emission gun (FEG), under an accelerating voltage of 200 kV. Dark field images of the ordered phases (bcc\textsubscript{B2}+bcc\textsubscript{D0\textsubscript{3}}) were obtained using (100) diffraction spots that belongs both to the bcc\textsubscript{B2} and bcc\textsubscript{D0\textsubscript{3}}(200). A typical TEM dark field image of Fe-6.5 wt.% Si under wheel speed of 30 m/s is shown in Fig. 1, with the selected area electron diffraction pattern shown in the inset. The measurements of the antiphase domain size (\textit{r}) were carried out using linear intercept method with the help of imageJ software. The red arrowed line in Fig. 5.1 shows a typical measure of 2\textit{r}. The averaged value of all the measured \textit{r} is taken as the domain size. (It should be noted that (001) spot can not be used to determine the bcc\textsubscript{B2} domain size, if there is a mixture of bcc\textsubscript{B2} and bcc\textsubscript{D0\textsubscript{3}} phases.) The measured cooling rate and domain size at each wheel speed are listed in Table 5.1.
Fig. 5.1 Dark field TEM image of Fe-6.5 wt.% Si melt spun ribbon at a wheel speed of 30 m/s. The inset is the corresponding selected area electron diffraction pattern, where the B2(100) spot was used for obtaining the dark field image.

Table 5.1. Summary of cooling rate and bcc_B2 domin size of Fe-6.5 wt.% Si at each wheel speed.

<table>
<thead>
<tr>
<th>Wheel speed, m/s</th>
<th>3</th>
<th>5</th>
<th>7</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling rate, K/s @ 1173 K</td>
<td>36219</td>
<td>104896</td>
<td>16770</td>
<td>34919</td>
<td>67060</td>
<td>79844</td>
</tr>
<tr>
<td>Domain Size, nm (Experimental)</td>
<td>-</td>
<td>22±8</td>
<td>15±3</td>
<td>10±2</td>
<td>8±2</td>
<td>5±2</td>
</tr>
<tr>
<td>Domain Size, nm (Modeling)</td>
<td>40</td>
<td>23</td>
<td>17</td>
<td>11</td>
<td>7</td>
<td>6</td>
</tr>
</tbody>
</table>

5.3. Thermodynamic and kinetic analysis

There are two distinct physical cooling periods in the melt spinning process, the wheel-contact period and the free-flight period [209]. In the first stage, the ribbon is in intimate contact with the quench wheel and cooled by the heat conduction across the ribbon-wheel boundary. In the later stage, the ribbon separates from the wheel, and the cooling rate is determined by radiation and convection in the chamber. The first stage thus contains the rapid solidification of the Fe-Si alloy melt and followed by a quench process of the ribbon. The second stage is solely a quenching
process. It is known that the final microstructure may be a bcc_B2 structure with well-developed or undeveloped antiphase domains, or bcc_B2 and bcc_D0_3 mixture depending on the cooling rate [58, 68]. This can also be seen from the Fe-rich Fe-Si phase diagram [215] as shown in Fig. 5.2. (The phase field between bcc_A2 and bcc_B2 two phases shown in Fig. 5.2 may cannot represent the exact experimental one. However, this will not affect the analysis work within the present paper.) The equilibrium phase of Fe-6.5 wt.% Si at room temperature is bcc_D0_3.

![Fig. 5.2 The Fe-rich Fe-Si phase diagram [215]. The red line indicates the alloy composition of Fe-6.5 wt.% Si. Tx is the bcc_A2/bcc_B2 transition line, Ty is the bcc_B2/bcc_D0_3 transition line, Tc is the magnetic transition line, and T0 is the line where liquid and bcc_A2 have equal Gibbs free energy.](image)

**5.4. CALPHAD data**

As an initial step, the solidification behavior of this alloy was examined using the DICTRA module in the ThermoCalc software [216]. To understand the solidification behavior of Fe-6.5 wt.% Si alloy, we need necessary thermodynamic and diffusion mobility data as input. Thermodynamic descriptions for the Fe-Si system are readily available in the literature [215, 217].
In the kinetic part, the atomic mobility parameters of bcc_A2 and liquid were assessed by Wang et al. [218, 219]. However, those for the bcc_B2 and bcc_D03 phases are unavailable in the literature. As a preliminary work, the atomic mobilities of the bcc_B2 phase were assessed. It is known that the composition dependence of each atomic mobility parameter for a binary solution expressed in the form of Redlich-Kister polynomial is [220, 221]:

$$\Phi_i = \sum_p x_p \Phi_i^p + \sum_p \sum_{q>p} x_p x_q \left[ \sum_{r=0}^{m} r \Phi_i^{p,q} (x_p - x_q)^r \right]$$

(1)

where $\Phi_i$ represents the activation energy $-Q_i$ or the scaled frequency factor $RT\ln M_i^0$, $\Phi_i^p$ is the value of $\Phi_i$ for element $i$ in pure element $p$. $r \Phi_i^{p,q}$ is the adjustable interaction parameter, and $x_p$ is the mole fraction of element $p$. Helander et al. [222] considered the contribution of chemical ordering (bcc_B2 ordering) on atomic mobility phenomenologically by generalizing the Girifalco model [19]. The activation energy can then be expressed as:

$$Q_i = Q_i^{dis} + Q_i^{ord}$$

(2)

where $Q_i^{dis}$ is the contribution from the disordered state and can be expressed as Eq. (1), while $Q_i^{ord}$ presents the contribution from chemical ordering. This quantity is given by an equation in the form:

$$Q_i^{ord} = \sum_p \sum_{q>p} Q_i^{p,q} \left[ y_p^\alpha y_q^\beta - x_i x_j \right]$$

(3)

where $Q_i^{p,q}$ is a parameter describing the contribution of the component $i$ due to the chemical ordering of the $p$-$q$ atoms on the two sublattices $\alpha$ and $\beta$, $y_p^\alpha$ is the site fraction of component $p$ on the $\alpha$ sublattice. This model was originally developed for bcc_B2 ordering, which is suitable for the current situation. As the atomic mobilities of bcc_A2 and liquid optimized by Wang et al. [218, 219] are compatible with the thermodynamic description by Lacaze and Sundman [217], the ordering contribution of the atomic mobility was also optimized in the present work using the thermodynamic factors computed from ref. [217] for consistency. The $Q_i^{dis}$ part is taken form ref. [218] directly. According to ref. [217], the bcc_B2 phase was modeled with a sublattice model (Fe, Si)$_{0.5}$(Fe, Si)$_{0.5}$, only four ordering parameters were thus optimized for atomic
mobilities: \( Q_{Si}^{FeSi} = Q_{Si}^{Si:Fe} = -62000 \) and \( Q_{Fe}^{FeSi} = Q_{Fe}^{Si:Fe} = -95000 \) (all in J/mol). It should be noted that, for simplification, only the experimental interdiffusivities measured by Rabkin et al. [224] and Heikinheimo et al. [225] were considered in the present work. The model-predicted interdiffusivities in the temperature range of 1006-1483 K are compared with the related experimental data from Rabkin et al. [224] and Heikinheimo et al. [225] in Fig. 5.3 with satisfactory agreement. A constant value of \( M \) was added to separate the data. The ordering effect on diffusivity is clearly seen as indicated by the dotted line in the figure. Thus, these atomic mobilities are reliable for the subsequent kinetic calculations.

Fig. 5.3 Model-predicted interdiffusivities (solid lines) of Fe-Si solid solution along with the experimental data (symbols).

5.5. Solidification simulation

The bcc_D03 phase was neglected in the thermodynamic description from Lacaze and Sundman [217]. However, this does not affect the prediction of the bcc_B2 and bcc_D03 phase formation during solidification, since the liquid composition can be an effective indicator for the ordered phase formation. For example, when the liquid composition reaches 22.67 at.% Si during
solidification, there will be bcc_B2 formation from liquid under local equilibrium assumption. The bcc_D0₃ order contribution to diffusion is thus not necessary and neglected.

In the route of solidification simulation, the temperature of Fe-6.5 wt.% Si was set to the present experimental condition (1863 K) which is above the liquidus temperature 1698 K. The simulation time was controlled for each cooling rate to ensure the complete solidification, i.e. the fraction of solid reaches 1. A double geometry was used in all the solidification simulations. (For more details of double geometry, the readers can refer to DICTRA Manual.) The half of secondary dendrite arm spacing value should be reasonably used as the length of simulation region. However, the secondary dendrite arm spacing value is difficult to measure in the current melt spinning experiments due to the extreme cooling rate and very thin film produced. Thus, before simulating the experimental cooling rate, the effects of half of secondary dendrite arm spacing and cooling rate on Si concentration in liquid was tested. A series of simulations was carried out at a cooling rate of 10⁵ K/s with varying half of secondary dendrite arm spacing from 1.8×10⁻⁶ m to 1.0×10⁻⁹ m. The final Si concentration in liquid decreases from 17.76 at.% to 14.53 at.% as half of secondary dendrite arm spacing reduces. In another series of simulations, the half of secondary dendrite arm spacing was kept as 2.0×10⁻⁴ m and the cooling rate was treated as a variable from 1 to 11 K/s. The Si pile up in liquid has a maximum of 17.76 at.% when the cooling rate is 5 K/s in this case. From these two series of simulations, the Si concentration in final liquid is critically related to cooling rate and secondary dendrite arm spacing. A smaller secondary dendrite arm spacing makes the solute concentration in the final liquid less deviate from the original melt. In other words, it causes smaller segregation. Secondary dendrite arm spacing is inversely proportional to cooling rate (at least in low cooling rates) and is also composition dependent [226]. Then, the simulations for the real cooling rates measured in the present work are carried out using reasonable half secondary dendrite arm spacings. The simulated solidification paths at each cooling rate are presented in Fig. 5.4.
Fig. 5.4. Simulated solidification paths of Fe-6.5 wt.% Si under different cooling rates and half secondary dendrite arm spacing $\lambda$.

Here, we made a presumption that DICTRA is reliable to perform solidification simulation at high cooling rates. The cooling rate, half secondary dendrite arm spacing denoted as $\lambda$, and the final liquid solute concentration in at.% are also indicated in Fig. 5.4. The equilibrium calculation based on the lever rule is also shown in the figure for reference. The simulation results show that the composition of the final liquid become less and less Si rich (17.75 to 14.80 at.%). So, there is less and less solute redistribution as cooling rate increase. The liquid composition never reaches 22.67 at.% Si at which the bcc_B2 phase starts to form as a primary phase. Thus, it can be concluded that the ordered phase does not form during the solidification process but forms in the subsequent quenching process. The simulation results indicate that there is a certain segregation of the solute element and no solute trapping happen even at the cooling rate of $10^7$ K/s. This could be due to the fact that DICTRA calculation is based on local equilibrium assumption, solute trapping can seldomly happen. In reallity, when the phase interface mobility reaches the diffusivity of solute in liquid, there will be solute trapping [227]. In other words, when the liquid is supercooled below the T0 line, the diffusionless phase transition might happen. The micro-
composition of Fe-6.5 wt.% Si melt spun should not deviate much from the overall composition according to the above simulation. For example, the simulated time dependent concentration profiles of Fe-6.5 wt.% Si at the cooling rate of 36219 K/s are shown in Fig. 5.

![Graph showing concentration profiles](image)

Fig. 5.5 Simulated time dependent concentration profiles along half secondary dendrite arm spacing of 3 μm in Fe-6.5 wt.% Si alloy under a cooling rate of 36219 K/s.

In this case, the solidification process only takes about 0.0064 s. Apparent solute pile up in liquid near the propagating solid/liquid interface can be seen from the concentration profiles at time 0.0048 s, 0.0052 s, and 0.0056 s. The Si concentration in primary solid phase also increases with time due to diffusion. The solid concentration in the front and end of the solidification distance has a difference of about 3.4 at.% immediately after solidification complete. However, this difference shrinks quickly in the subsequent quenching process due to high temperature solid state diffusion, see Fig. 5.5. The inhomogeneity almost disappears at time 0.016 s when the alloy temperature (1283 K) is above the bcc_A2/bcc_B2 transition temperature. Our simulation results indicate that Fe-6.5 wt.% Si alloy will be even more homogenized at high cooling rates due to diffusion and the initial liquid temperature also shows positive correlation with the homogeneity of melt spun.
5.6. Growth of the bcc_B2 antiphase domain

In the subsequent modeling process, the alloy composition was assumed to be unchanged. As indicated by the phase diagram shown in Fig. 5.2, when the temperature decreases to the bcc_A2/bcc_B2 transition line, the disordered bcc_A2 phase completely loses its stability and the ordered bcc_B2 phase forms through the second-order transition. Due to the second-order transition, the formation of bcc_B2 from bcc_A2 is not a classical nucleation and growth phase change [228]. The microstructure is quite similar to spinodal decomposition, but the order parameter is not conserved. A second-order phase transition is more reasonably described as an antiphase domain growth process [229, 230]. It is known that bcc_B2 has two sublattices (Fe, Si)_0.5(Fe, Si)_0.5 as discussed above. Si may prefer the first or second sublattice, and thus induces two ordered components. As the temperature reached the critical temperature, the long-range-ordering parameter, η, is close to the equilibrium value ±ηl in each domain, but the overall long-range order is still zero [231]. The kinetics of ordering consists of swelling of the web-like regions of both types and an increase in their correlation radii as the boundaries of these regions move in a way that the total volumes of the ordered components is kept the same. In the early work, English [232] studied the bcc_B2 domain growth in Fe-Co-2V alloys using X-ray diffraction and found that the domain size is proportional to t^{1/2}. Later, Allen and Cahn [229] developed a microscopic diffusional theory for the antiphase boundary motion. The driving force for the microstructure evolution is related to the curvature of the antiphase boundaries, which reduces during microstructural evolution [229, 230]. According to Allen and Cahn [229], the surface area of the antiphase domain in a unit volume of a specimen, S_v, has the following relationship with the averaged square mean curvature $K_m^2$:

$$\frac{dS_v}{dt} = -MK_m^2 S_v$$

(4)

where t is time in seconds, $M$ is the coefficient equals to $2\kappa\alpha$, and $\kappa$ is the gradient energy coefficient, and $\alpha$ is the positive kinetic coefficient in the Allen-Cahn evolution equation. Allen and Cahn in [231] modelled the isothermal domain growth using variable $S_v$. We intend to model the domain size evolution instead. For bcc_B2 domain growth, Allen and Cahn [229] also derived the following relation: $K_m^2 = \epsilon S_v^2$, where $\epsilon$ is a constant. Considering $K_m^2$ is inversely proportional to the square of averaged domain size $r^2$, we transform Eq. (4) as:
\[ \frac{dr^2}{dt} = k(T(t)) \]  

(5)

where \( k(T) \) is the temperature-dependent coefficient. Then, the isothermal domain size growth follows the parabolic law:

\[ [r(t)]^2 - [r(0)]^2 = k(T)t \]

(6)

where \( r(0) \) is the domain size at time 0. For varying temperature, integral of the Eq. (5) reads:

\[ r(t) = \left\{ [r(0)]^2 + \int_0^t k(T(t))dt \right\}^{\frac{1}{2}} \]

(7)

To model the continuous growth of the aniphase domains during rapid quenching, the kinetic coefficient \( k \) can be treated as:

\[ k(T) = e^{f(T)} \text{ with } f(T) = a + bT + cT\ln T + dT^2 + eT^{-1} \ldots \]

(8)

where \( a, b, c, d, \) and \( e \) are coefficients to be determined. Depending on the experimental data, one can choose more or less coefficients in Eq. (8).

Time, temperature, and cooling rate \((-\dot{T} > 0)\) are correlated during the quenching process. Since the melt spinning process considered in the present work is quite rapid, and due to lack of the detailed modeling of this process, it is reasonable to operate with constant averaged cooling rates depending on rotation speed of the wheel. If we further neglect the incubation time for bcc_A2 to bcc_B2 phase transformation, then \( T = T_s + t\dot{T} \), where the transformation temperature \( T_s \) is 1039 K for Fe-6.5 wt.% Si [11]. If the domain growth end temperature is \( T_f \), the total time for domain growth is \( t_g = (T_f - T_s)/\dot{T} \). Since exact growth end temperature is unknown and exponential character of the function \( k(T) \) can provide vanishing growth rate at low temperature, we consider \( T_f \) to be room temperature 298 K.

Radius \( r(0) \) is the domain size at critical temperature and it is also the final domain size at infinite cooling rate, when growth is absent. We assume \( r(0) = 0.2854 \) nm, the lattice parameter of Fe-6.5 wt.% Si at room temperature [233]. In addition, the bcc_D03 ordered phase formation
was neglected due to the technical difficulty in distinguishing it from bcc_B2 and measuring its phase fraction in the melt spinning samples.

Since there are no experimental isothermal domain growth kinetic data in the literature, the model was solely calibrated using the measured cooling rates and domain sizes in the rapid quenched samples as listed in Table 1. To make an approximation simpler and more practical, we leave just two coefficients, $b$ and $e$ in function $f$ and make $b$ linearly dependent on the cooling rate. Thus, $f(T, \dot{T})$ is approximated as:

$$f(T, \dot{T}) = (10^{-9}\dot{T} + 0.0232)T - 10000T^{-1}$$  \hspace{1cm} (9)$$

when $|\dot{T}| > 10^5 \text{ K/s}$ the cooling rate affects function $f$. The simulated domain sizes of bcc_B2 with different cooling rates are shown in Table 5.1 and Fig. 56.

![Model-predicted domain size as a function of cooling rate.](image)

The experimental data are reasonably reproduced. As the quenching rate increases, the domain size converges to $r(0)$. This happens practically at a cooling rate of $7\times10^6$ K/s. Based on the present modeling, the bcc_B2 domain size is comparable with the anti-phase boundary
thickness of 2 to 3 nm [30] at a quenching rate of 2 to $3 \times 10^6$ K/s. However, due to slow reduction in the domain size at high cooling rates, a cooling rate of $10^6$ K/s producing domain size of 5 nm would be optimal.

While the model is based on extrapolation of experimental data for higher cooling rate, it is still reliable, because it includes asymptotic value for the infinite cooling rate. It should be noted that the currently obtained function $f(T, \dot{T})$ is only reliable for the high cooling rate probably $>1000$ K/s.

It is known empirically that the higher the cooling rate is the higher the ductility of the Fe-6.5 wt.% Si can be reached. We can rationalize this as follows. Ordered bcc_B2 and bcc_D03 phases are brittle, while disordered bcc_A2 is ductile. Antiphase boundaries between different bcc_B2 domains cannot be well ordered. Thus, they are disordered and similar to disordered bcc_A2 phase and are ductile. The anti-phase boundary thickness is 2 to 3 nm [234]. Thus, the smaller size of the bcc_B2 domains, the larger volume fraction of the ductile disordered antiphase boundaries will be contained in the material, and the more ductile the resultant multiphase material is.

5.7. Conclusions

Phase transformations during melt spinning of Fe-6.5 wt.% Si electric steel were analyzed using thermodynamic and kinetic calculations. Rapid solidification cannot be used to quench bcc_A2 as the final phase due to the second-order feature of bcc_A2/bcc_B2 phase transition. There is no bcc_B2 phase formation in the solidification stage of the melt spinning, and the composition of the melt spun shows no apparent inhomogeneity due to high temperature diffusion. The bcc_B2 phase forms during the subsequent quenching process. The domain growth during quenching process was described using the Allen-Cahn theory. Increase the quenching rate can decrease the domain size. A cooling rate of $10^6$ K/s is necessary to suppress the bcc_B2 domain growth and produce a ductile material. Its ductility is provided by relatively large volume fraction of the ductile disordered antiphase boundaries between different brittle bcc_B2 domains.
CHAPTER 6 IN-SITU COOLING RATE ANALYSIS OF MELT-SPUN FE-6.5WT%SI USING THERMAL IMAGING TECHNIQUES

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Abstract

Measuring the temperature of a dynamic processes is difficult with the techniques requiring thermal contact. The advantages of using thermal imaging techniques to measure the cooling rates of ribbons undergoing melt-spinning are high sampling rate and complete data collection for the entire time of flight. Utilizing a thermal imaging camera, it is possible to observe the extreme cooling rates experienced during rapid solidification and calculate them by taking the slope of the cooling path measured. This work is to identify the cooling rates associated with various wheel speeds in an effort to take a process parameter and transform it into a process independent measurement.

6.1. Introduction

Measuring the cooling rates experienced during rapid-solidification processes is a difficult challenge to overcome. Traditional methods used to measure temperatures over time have certain limitations both in area data collection and temporal resolution of that data. Frequently used laboratory thermocouples can collect data from a single point and is representative of the area in the immediate vicinity of the thermal probe, subject to the thermal transfer properties of the material in question. Another instrument frequently used in temperature data collection is the optical pyrometer. It can collect data from a distance and do not need to be in direct contact with a sample to measure its temperature, though they do need to see the light being emitted by a radiating body to measure temperature so there is a limit to what temperatures can be obtained. Both of these methods have a similar problem however, in that their collect data on a very slow scale approximately 1 measurement every second. This presents a big problem when investigating the cooling rate of a process that takes only a couple seconds from start to finish.
The ideal temperature measurement method for studying rapidly occurring events needs to be able to measure the temperature of a large number of sample areas simultaneously and also be able to collect many data points per second. High resolution thermal imaging technique enabled by a state of the art FLIR thermal camera (A8303sc) satisfies both of these criteria. This advanced thermal camera is capable of capturing data at high resolution (1280 × 720 pixels) and at high refresh rate (60 Hz). With both of these capabilities this paper will attempt analyze the cooling rates of melt-spun Fe-6.5wt%Si at various wheel speeds.

There is a correlation between the wheel speed selected and the observed cooling rate, with higher wheel speeds corresponding to increased cooling rates. In this research it is assumed that the cooling rate of ribbon’s free surface will have lower cooling rate than its wheel side surface as majority of the cooling is achieved through radiant cooling while convective cooling is limited. In comparison, the wheel side of the ribbon will have conductive cooling through the copper wheel during the initial cooling stage. Once the ribbon is detached from the wheel, both surfaces are subjected to radiant and convective cooling. The detachment of ribbon from copper wheel occurs approximately two inches after the ribbon has moved from the footing area where the molten metal stream touches the wheel, then heads towards the collection drum. Because of the position and angle of the viewport in our melt-spin system, the thermal camera was not able to capture the cooling rate of the ribbon near the “foot” area, where the molten metal was going through the fastest cooling.

The reason that Fe-6.5wt%Si was selected for this study is twofold. The first is that Fe-6.5wt%Si is well suited for the melt-spinning process. In addition, it is well known that under slow cooling conditions the material retains is brittle nature; but when subjected to sufficiently high cooling rates, it transforms into an easy-to-handle ductile material. The objective of this work is to determine the critical cooling rate that can install sufficient ductility to the Fe-6.5wt%Si for mass production.

6.2. Method

The experiment was conducted using a melt-spinner in conjunction with a FLIR thermal Camera (A8303sc InSb (3.0 - 5.0μm)). The settings for the camera were to take a temperature reading at every pixel with a 1080p resolution at 60 Hz. For each melt-spin run, approximately 6
gram of Fe-6.5wt%Si was drop-cast into a 1 cm diameter cylinders and clipped to length using bolt cutters. The samples were wire-brushed to remove any surface oxide. They were then loaded into a quartz crucible with a 0.81 mm diameter orifice. The weight of both the sample and the crucible were recorded and then loaded into the melt-spinner. The height of the nozzle from the copper wheel was set to 7 mm in order to provide a stable melt pool and avoid splatter and arcing to the induction coil. The crucible and chamber were then evacuated and refilled with 1/3 atm of He as an inert atmosphere. After the copper wheel reached the desired speed, induction coil was energized and sample was quickly heated up. An optical pyrometer was used to measure the temperature of the crucible and once it had reached a temperature of 1590 °C the recording began and an ejection pressure of 120 Torr was applied to the crucible and the molten metal was ejected onto the rotating copper wheel. It solidified into a thin ribbon and quickly cooled down.

The thermal camera is set up directly in line with the path of the ribbon through the melt-spinner looking down into the chamber at a 45-degree angle as shown in Figure 6.1. Sapphire was used as the window material on the Lexan viewing port as sapphire is transparent in the infrared spectrum at which the camera uses to record temperatures.
After cooling profiles were collected, cooling rate can be constructed by taking the first derivative of the thermal profile with respect to time. Since it was impossible to view the same area of the same ribbon in two frames, an indirect method for calculating the cooling rate was devised. This method took advantage of the fixed geometry between the orientation of the ribbon and the camera. A correlation between a pixel location and its physical distance from another pixel can be calculated. This correlation is a correction factor that will be used in the final calculation of cooling rate. The final requirement to calculate cooling rate was to define a thermal profile for each wheel speed. Two points along the ribbons path beginning where the melt-spun ribbon first enters the view of the camera and ending where the ribbon exits the frame are defined. Then a straight line between the two points was drawn and the temperature profile along this line was

Figure 6.1: Diagram showing orientation of thermal camera to melt-spinning wheel.
plotted. The temperature profile was collected for each frame where the stream and ribbon were stable and their values averaged for each wheel speed. Calculating the final cooling rate combines temperature profile with the observed distance correction factor leading to a temperature vs distance traveled. Converting to a temperature vs time profile is done by dividing the distance traveled at the corresponding wheel speed. The slope of the temperature profile at any point yields the instantaneous cooling rate experienced during the melt spinning process. The equation for calculating this cooling rate is shown below in Equation 1.

\[
\text{Cooling Rate} = \frac{dT}{dt} = \frac{dT}{dx} \cdot v = \frac{\text{Temp}_2 - \text{Temp}_1}{(\text{Pixel}_2 - \text{Pixel}_1) \cdot C} \cdot \text{Wheel Speed}
\]

**6.3. Results**

The temperature profiles of each wheel speed is shown below in Figure 6.2.

![Temperature Profile of Melt-Spun Fe-6.5wt%Si](image)

**Figure 6.2: Cooling profiles of each wheel speed with respect to time.**

The instantaneous cooling rate of each wheel speed at 900 °C of each wheel speed was calculated and is shown below in Figure 6.3. The cooling rates shown in Figure 6.3 are commensurate with those found in previous studies.¹
6.4. Discussion

The obtained cooling profiles clearly show that faster cooling rates yielded higher cooling rates as can be seen by their larger slopes in the region of 1000 °C to 600 °C. This is consistent with the hypothesis presented at the beginning of this paper. Also it follows that as the overall temperature of the ribbon lowers, the cooling rate lowers. This is observed as a decrease in the slope at lower temperatures. The dramatic reduction in cooling rate below 600 °C is most likely caused by the material detaching from the copper wheel and the instability at low temperatures caused by the warping the ribbon as it travels through the air. The initial discrepancy of maximum temperature of the ribbon is most likely caused by the competing cooling forces and the fact that the initial contact area of the melt on copper wheel is blocked by the inducting coil. At higher wheel speeds the heat is rapidly removed from the ribbon by the wheel while at slower wheel speeds the radiative and convective cooling takes over before the ribbon comes into view. While at the middle speeds the ribbon moves into view before sufficient cooling has taken place resulting in the higher observed maximum temperatures.

Figure 6.3: Wheel speeds vs Cooling Rates of melt-spun Fe-6.5wt%Si

![Graph showing wheel speeds vs cooling rates](image)
The most important temperature ranges for cooling rate analysis of Fe-6.5wt%Si is the 900-700 °C window as this is the temperature range where the transformation from a brittle to a ductile phase occurs and has the most stable temperature gradient. When calculating the cooling rate in this window it is likely that the observed cooling rate is representative of the entire sample, and could be used for future investigations. While the temperature ranges both above and below that have issues in interpreting their data. The three competing cooling factors in the higher ranges will cause issues in determining accurate cooling rates and at the lower ranges the stability of the ribbon to remain pointed at the thermal camera will cause similar issues.

6.5. Conclusions

It has been shown that thermal imaging technique can be used to observe the entire melt-spinning process both in terms of area and number of frames. The calculated cooling rates for this material are on the order of 10^6 K/s which is consistent with the previous calculations. There are a couple improvements that can be made. The first would be to isolate the area of collection to just the area of interest. This would provide the option for higher frame rates but comes at the cost of pixel resolution. The second would be to attempt to block all possible reflections from adding signal interference with infrared blocking materials.
CHAPTER 7 DETERMINING B2-DO3 ORDERING IN AN FE-6.5WT%SI ALLOY

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Abstract

Fe-6.5wt%Si steel surpasses the current extensively used Fe-3.2wt.%Si steel in lower iron loss, higher permeability, and near zero magnetostriction. As a cost effective soft magnetic material, Fe-6.5wt%Si may find applications in motors, transformers, and electronic components. However, the brittleness of the alloy poses processing challenges. The brittleness in Fe-6.5wt%Si is attributed to the formation of ordered phases. Evaluation of the amount of ordered phases is important for the research and development of Fe-6.5wt%Si. In the current study, Fe-6.5wt%Si samples were prepared by melt spinning with various wheel speeds. The varying wheel speed changes the cooling rate, which was measured precisely via thermal imaging. Two quantitative methods have been investigated to estimate the ordering degree presented in the Fe-6.5wt%Si samples along with TEM and normal theta-2theta X-ray diffraction methods. One method is based on rotating crystal XRD technique, and the other is magnetic thermal analysis technique. These two methods effectively quantified the varying degree of ordering presented in the samples and were deemed more suitable than the TEM, normal theta-2theta XRD methods for Fe-Si due to their ease of sample preparation and short turn-around time.

7.1. Introduction

Fe-Si alloy, or so called electric steel or silicon steel, has been the primary material for the low frequency soft magnetic applications since it was first developed more than 100 years ago [42]. Nowadays, the market share of Fe-Si accounts for almost half of the total market share of soft magnetic materials [25]. Fe-Si is especially popular in the application of motors, generators, transformers, and inductors [41]. The success of Fe-Si originated from the combination of favorable magnetic, electrical and mechanical properties. Fe-Si is a type of magnetic material that contains primarily iron and silicon, where silicon is present in a few weight percent as an alloying
element. The direct effect of silicon alloying in iron is the improvement in electric resistivity [19], which is essential to reduce eddy current loss at higher frequencies. The ductility of Fe-Si is also increased by a minor addition of silicon compared to pure iron due to suppression of the α to γ phase transition in iron, allowing Fe-Si to be cold-rolled into thin sheets [25]. Silicon addition also results in reduction in magnetic anisotropy and the magnetostriction of iron, which leads to higher permeability and lower noise and vibration. Silicon concentration has been held to around 3.2% (all compositions are expressed in wt.% in this paper) by manufacturers, following the practice developed by Robert Hadfield in 1900 [19].

Further increase in silicon content results in a further increase in electric resistivity, making high silicon steel more favorable for higher frequency applications [236]. It was found that 6.5%Si addition is especially attractive due to its high permeability, zero magnetostriction, and low iron loss. It should also be noted that the increase in silicon also results in unfavorable change of properties, such as lower magnetic saturation, lower Curie temperature, and formation of ordered intermetallic phases. Additionally, Fe-6.5%Si lacks sufficient ductility to be processed by existing manufacturing processes, i.e. cold rolling. The brittleness of Fe-6.5%Si originates from the formation of the ordered phases. The ordered phases form due to the preferred pairing of iron and silicon atoms when silicon concentration is increased. In the traditional Fe-3%Si low silicon steel, silicon atoms distribute randomly into the body centered cell of iron atoms across all temperatures up to melting point. When silicon content increases beyond ~5%, nearest neighbor pairing occurs, resulting in the formation of B2 phase [58, 59]. Further increase in silicon content beyond 6% results in additional next-nearest-neighbor pairing, forming D0₃ phase. The presences of ordered phases interact with the dislocations resulting in a strengthening effect, and dramatically reduces the ductility of the alloy.

To prepare ductile thin sheet of Fe-6.5%Si for soft magnetic applications, the ordered phases have to be suppressed. A few processes that utilize the far from equilibrium process were found successful in the lab scale, including thermomechanical processing [115, 122], rapid solidification [49, 50, 66, 88, 130, 206], and deposition/diffusion annealing [35, 137, 144]. These processes were only possible because the formation of ordered phases was carefully controlled. The amount of ordered phases, or ordering degree is therefore vital for the success of Fe-6.5%Si production, and should be a parameter closely monitored. However, normal x-ray diffraction using
the Bragg-Brentano geometry does not work well in the quantification of these phases due to the low intensities of the superlattice peaks belonging to the ordered phases. Transmission Electron Microscopy (TEM) Selected Area Diffraction (SAD) along certain zone axes can be used qualitatively to visualize the occurrence of ordered phases, but the diffraction spots lack the quantitative information. In addition, the high cost and long time of TEM sample preparation prohibit a large number of Fe-6.5%Si samples to be examined on a regular basis. The current study validated two methods that can efficiently identify the ordering degree in melt-spun Fe-6.5%Si. One is rotating crystal transmission XRD, and the other is thermogravimetric analysis with applied magnetic field (M-TGA). A number of samples with varying degree of ordering were prepared by melt spinning with various wheel speeds while keeping all other parameters constant. The ordering degree was quantified by the rotating crystal XRD method and the M-TGA method. The occurrence of ordered phases was also examined by TEM SAD technique, and correlated with the proposed quantitative characterization methods.

7.2. Experiments

The Fe-6.5%Si samples for this study was prepared by melt spinning. Prior to the melt spinning, the samples were alloyed by arc melting and drop casted into ~6 gram cylindrical shots. The melt spinning was performed in a vacuum chamber partially filled with 1/3 atm of ultra high purity helium. The sample was heated to 1590°C in a quartz crucible before it was ejected through a 0.81 mm precision orifice onto a 2.5 cm wide by 25 cm diameter copper wheel using 120 Torr overhead pressure. The temperature of the melt was monitored by two color optical pyrometer. The wheel speed of the copper wheel was precisely controlled and monitored by motor control system. Wheel speeds of 1 m/s, 3 m/s, 5 m/s, 7 m/s, 10 m/s, 20 m/s and 30 m/s were used to prepare the samples with varying degrees of cooling. A thermal camera, FLIR A8303sc, was set up to record the ribbon surface temperature through a sapphire window during the melt spinning process. The thermal camera has a frame rate of 60.9 Hz, a resolution of 1920 x 1080, and a pixel size of 0.7 mm. For each frame, a thermal profile between two points of 500°C and 1300°C along the ribbon is obtained. This spatial thermal profile was then converted to a temporal thermal profile by converting the pixels to distance, then the distance to time. A single cooling rate was calculated
for each frame assuming a linear change in temperature from the thermal profile. Multiple frames were used to acquire the average cooling rate for each wheel speed.

XRD patterns of the samples were collected from the ribbon using Cobalt radiation via the Bragg Brentano geometry with a Philips PANalytical X-Pert Pro diffractometer. The samples were placed on a zero-background sample holder for improved signal quality at low 2theta angles.

High-energy X-ray diffraction was conducted at the Advanced Photon Source (APS) of Argonne National Laboratory at beamline 6-ID-D. A GE amorphous silicon detector with 2048x2048 pixel array (200x200 μm² pixel size) was positioned 1159.5 mm behind the sample to collect 2D diffraction patterns. Monochromatic X-rays with energy of 100.25 keV (corresponding to a wavelength of 0.12365Å) were used for the experiments that were performed in transmission mode. For each wheel speed, five samples were stacked and secured against a hole in an aluminum plate where the incident beam passes through. The exposure time for each specimen was 0.5 seconds. The relative intensity versus scattering vector Q plot was generated integrating the 2D patterns acquired over the entire 360°. Lamellae for TEM were lifted out from the wheel side of the samples by focused ion beam (FEI Helios NanoLab Dual-beam). TEM (FEI Tecnai G2-F20) selected area diffraction was performed under the accelerating voltage of 200 kV with a field emission gun along the <110> zone axis.

The rotating crystal transmission XRD was done on a single crystal x-ray diffractometer (STOE IPDS, STOE & Cie GmbH) with Molybdenum source. A collimated X-ray beam with a spot size of 0.5 mm was used to irradiate the sample, and a 2D image plate was used to collect transmitted diffracted x-rays. The sample was mounted in the eccentric point of an Eulerian cradle. The ω angle was changed from 0 to 180° during the 10 minute scan, while the X-ray tube and the image plate stayed stationary as shown in Figure 7.1. The intensities of the rings were then integrated over the entire circle to generate the intensity versus 2θ plot for evaluation of relative intensities.

Thermogravimetric analysis was done using a Netzsch STA instrument with two magnets mounted beneath the sample pan. The magnets attract the sample adding to the apparent weight measured by the balance below the sample pan. The samples were heated to 800°C then cooled to room temperature with the heat/cool rate of 10°C/min.
7.3. Results and discussion

7.3.1. Cooling rate analysis

By tuning the wheel speed, a number of different extent of cooling has been achieved. According to the thermal imaging data acquired, the cooling rates decrease with decrease in wheel speeds, and range from $10^6$ K/s for 30m/s samples to $10^4$ K/s for 3m/s samples. The cooling rates match well with the rates reported earlier on Fe-Si-B alloy using the same instrument where the cooling rates were $5.2 \times 10^6$K/s at 20m/s and $4.5 \times 10^5$K/s at 5m/s wheel speeds. The average cooling rate experienced by the ribbon can be expressed by the following equation [210]:

$$\frac{dT}{dt} = h \left( T_i - T_w \right) / x \rho c_p$$ (1)

where $h$ is the heat transfer coefficient, $T_i$ is the initial temperature of the ribbon and $T_w$ is the temperature of the wheel, $x$, $\rho$ and $c_p$ are the thickness, density and heat capacity of the ribbon formed respectively.

For a given material, the cooling rate is controlled by thickness $x$ and heat transfer coefficient $h$. The thickness $x$ is dependent on the wheel speed $v$ by volumetric flow rate of the melt from the nozzle $Q$ according to [210]

$$\frac{x^2 v}{Q^{1/2}} = constant$$ (2)
With the charge mass, melt temperature, melt spun tube orifice diameter, ejection pressure, and chamber pressure held constant, the volumetric flow rates $Q$ for all melt spinning runs remain the same. According to equation (2), changing the wheel speed results in the change in thickness of the ribbons. The change in thickness of the ribbons, in turn, results in change in the cooling rates obtained according to equation (1). Changing the wheel speed effectively alters the thickness of the acquired ribbon [210] as shown in Figure 7.2. The change in thickness of the ribbons results in an expected change in the cooling rate.

![Figure 7.2. Plot of ribbon inverse thickness (left) and the cooling rate (right) as a function of the wheel speed.](image)

**7.3.2. θ - 2θ XRD analysis:**

The $θ - 2θ$ scan XRD patterns are shown in Figure 7.3. The patterns reveal the major peaks belonging to the body centered cubic (BCC) crystal lattice that is present for all the three phases. In Fe-6.5%Si, all three phases A2, B2, D0$_3$ share the body centered (or the like for D0$_3$) crystal structure. A2 is the solid solution phase, where the Fe and Si distribute randomly in all the BCC lattice sites. As a result, the only allowed reflections in the XRD pattern for A2 phase are the planes that have the sum of miller indexes to even number. Nearest neighbor pairing results in the formation of B2 phase. Due to the dissimilar atoms present in the BCC lattice, forbidden planes start to appear in the XRD pattern such as (100) planes at $\sim 37.12°$ 2$θ$ angle using Co radiation. In addition to the ordering present in B2, further ordering between the next-nearest-neighbor atoms results in the formation of D0$_3$ phase, which has unique superlattice planes (111) and (200).
appearing at the 2θ angle of 31.74° and 36.82° in the Co radiation XRD pattern. One can think of a superlattice structure consisting of 16 atoms from 8 BCC cells piled together to better understand the B2 and D0₃ ordering phenomena [237]. B2 ordering occurs when the atomic percentage of Si is 6.25 at% where there will be 1 silicon atom in the 16-atom superlattice structure. The silicon atom tends to occupy one of eight body centered sites on this superlattice with the formula of Fe₁₅Si₁. D0₃ ordering occurs when the atomic percentage of Si is 12.5 at% where there will be two silicon atoms in the 16-atom superlattice structure. The two silicon atoms are likely to occupy two of the eight body centered sites to the next-nearest-neighbor on this superlattice with the formula of Fe₁₄Si₂. Fe-6.5wt%Si alloy lies in the two phase region between B2 and D0₃ below its Curie temperature.

Comparing the major peaks, these superlattice peaks have small intensities, being less than 3% for B2, and less than 6% for D0₃. Using the normal θ - 2θ XRD technique is, therefore, difficult to quantify the amount and even the presence of B2 and D0₃, especially for rapidly quenched samples. The XRD patterns have been refined for the BCC crystal lattice parameters. The lattice parameters stay around 2.854 to 2.856 Å, matching the values fitted for 6.5% silicon steel [238, 239]. It was shown that rapid solidification may result in expansion of the crystalline lattice compared with the corresponding equilibrium BCC lattice [238]. However, the cooling rates achieved in the melt spinning process in this study do not seem to systematically affect the BCC crystalline lattice parameters.

Efforts have been made to identify the presence of B2 and D0₃ with prolonged scans of the superlattice region in the XRD patterns as shown in Figure 7.3b. After the extended XRD scans using the high resolution setting, the superlattice peak belonging to both B2 and D0₃ at ~37° 2θ can be observed for 3m/s and 5m/s, but not for the other samples prepared at higher wheel speeds. Characterization of ordering in samples prepared using wheel speeds higher than 5m/s is beyond the limit of the current technique. There have been attempts to use XRD to quantify the ordering degree in Fe-6.5%Si the literature [208, 240]. However, most of the studies were done in heat treated samples where a large amount of ordered phase was present. In addition to limited intensities revealed, the presence of preferred orientation can further add difficulties to observe the superlattice peaks. In the θ - 2θ XRD set up, the sample is usually lying flat on the sample stage. The stationary sample position defines the stationary sample orientation, therefore the XRD pattern
inevitably contains texture information which could significantly affect the relative intensities of each peak observed.

Figure 7.3. (a). Full XRD scan of samples melt-spun at different wheel speeds and (b). 30-40 degree local extended time XRD patterns.

7.3.3. TEM selected area diffraction analysis

TEM selected area diffraction (SAD) has been presented by a number of works [58, 67, 241, 242] to identify the presence of B2 and D0₃ superlattice ordering. In TEM, if the specimen is tilted along the <110> zone axis, the characteristic diffraction spots belonging to B2 (200), D0₃ (200), and D0₃ (111) may appear as shown in Figure 7.4f. The appearance of the red (111) spots is therefore correlated with the presence of D0₃ ordering. The (200) spots belong to both B2 and D0₃. The (200) spots can be used for the characteristic diffraction spots for B2 ordering only when D0₃ (111) spots are not present. In Figure 3, the SAD patterns for the samples melt-spun at a number of wheel speeds are shown. The D0₃ characteristic diffraction spots are only present in the low wheel speed samples, and start to disappear for wheel speeds higher than 10 m/s. B2 superlattice spots are faded but still present even in the sample melt-spun at 30m/s. It is apparent that the wheel speed controls the varying degree of order in the samples, where D0₃ is fully suppressed and B2 is partially suppressed for the sample melt-spun at 30m/s. This result is consistent with the study reported by Viala et al. [67] and Ouyang et al. [50].
Figure 7.4. <110> TEM selected area diffraction patterns of the samples melt-spun at different speeds (a) 1 m/s; (b) 5 m/s; (c) 7 m/s; (d) 10 m/s; (e) 30 m/s; (e) simulated SAED patterns indexing the spots belong to A2, B2 and D0\textsubscript{3} phases.

7.3.4. Synchrotron transmission XRD analysis

The XRD patterns using the synchrotron radiation are shown in Figure 7.5. The high signal strength from the synchrotron source does increase the signal to noise ratio, as the (200) superlattice peaks belonging to B2 and D0\textsubscript{3} at Q ~ 22.2 nm\textsuperscript{-1} show up in the patterns. This superlattice peak is almost non-existence in the 30m/s samples and begins to gain intensity when the wheel speed is decreased, as can be seen in the regional plot in Figure 7.5b. The increase in the intensity of the superlattice peak suggests an increase in the ordering of the samples. It also indicates that the ordering reaches a maximum at 5 m/s then slightly decreases at 3 m/s. It should be noted that the relative intensities of the peaks in Figure 7.5 are greatly affected by the texture of the samples as the samples are positioned stationary and perpendicular to the incident beam. Therefore, the attempt to quantify phase fractions using relative intensities is not viable. In Figure
7.5a, the relative intensities for the first two major peaks, i.e. (200); (110), are around 0.6 for most samples, but for a randomly oriented sample this number should be 0.15 referring the Pearson crystal database (reference number 1522334). This suggests that the samples are mostly oriented with (100) out of plane texture. It appears that the orientation is so strong that the (111) peaks belonging to D\textsubscript{0\textsubscript{3}} (111) at Q = 19.2 nm\textsuperscript{-1} do not appear in the patterns for any of the wheel speeds.

Figure 7.5. XRD patterns of the samples melt-spun at different wheel speeds using synchrotron radiation, (a) relative intensities versus scattering vector in the 15-60 nm\textsuperscript{-1} range showing the main peaks; (b) regional plots showing the superlattice peaks.

7.3.5. Rotating crystal transmission XRD

TEM SAD is viable for identifying the presence of ordered phases. However, the diffraction spots do not contain enough information to quantify the amount of the ordered phases. In addition, TEM is also time consuming and cost ineffective. XRD using high energy X-rays such as synchrotron radiation seems plausible, but the access to such facility is limited. To investigate the amount of the ordered phases or the degree of order, a new method is needed. X-ray diffraction is a technique which can quantify the amount of phases present, but the limitations of the θ - 2θ method described above make it difficult for this purpose. In this study, rotating crystal transmission XRD has been adopted to study the degree of ordering present in these melt-spun ribbons.
The technique reported here uses Mo as the radiation source, which limits the fluorescence generated by the Fe-Si sample, resulting in a higher signal-to-noise ratio. A focused beam and 2D image plate detector in a transmission type geometry have been employed which minimizes the angular divergence and sample displacement errors, resulting in increased intensities at low angles. During the experiment, the specimen is also tilted continuously and the intensities recorded in the 2D image plate is integrated. The resulting 2D XRD ring patterns are shown in Figure 7.6 for a number of wheel speeds. In the 2D images, the appearance of D0₃ characteristic rings appearing in lower wheel speeds and disappearing in higher wheel speeds can be clearly observed. It is apparent that D0₃ appears when the wheel speeds are below 10 m/s, which is consistent with the TEM SAD results.

Integration of the diffraction rings results in 1 dimension relative intensity versus 2θ XRD pattern shown in Figure 7.7a. Since the entire Debye rings are used for intensity integration, the effect of texture is minimized. In fact, the relative intensity between the (200) and (110) peaks for these patterns are around 0.13-0.16, matching the values of a randomly orientated sample, which should be 0.15. The relative intensity of characteristic peaks can be used to quantitatively evaluate the relative amount of each phase present. It can be seen from Figure 7.7a that the intensity of the D0₃ (111) peaks continues to increase with lower wheel speeds, which indicates an increase in D0₃ ordering with a decrease in wheel speed. The long range order parameter (LROP) of the sample, shown in Figure 7.7b, can be obtained by taking the relative intensities of the D0₃ (111) and bcc (110) peaks, and comparing that to the relative intensities of the pure D0₃ (111) and D0₃ (220) peaks. LROP provides a quantitative estimation of the degree of order of the sample, which directly relates the amount of ordered phase present, and has been used by a number of researchers [208, 243]. It can be seen from figure 7.7b that the LROP for melt-spun Fe-6.5%Si remain around 0.2 for wheel speeds of 10 m/s and above, then quickly double to 0.4 for the 7 m/s sample. The LROP continue to rapidly increase until it reaches 0.9 and above for samples melt-spun at 3 m/s and 1 m/s. The increase in the intensities of superlattice peaks with decreasing wheel speeds is in good agreement with the synchrotron XRD results. The large jump in LROP from 5 m/s to 3 m/s is likely due to the instability of the melt pool when low wheel speed is used. The samples are mostly long ribbons for wheel speeds 5m/s and above, but become mostly splashes for 3m/s samples. The instability of the melt pool can result in large fluctuation in cooling rates as shown in figure 2 for 3m/s sample with large error bar. When the speed is decreased to 1m/s, the further instability of
the melt pool results in splashing and the formation of almost exclusively globular or spheres. The thick globulars or spheres allow sufficient time during the solidification and the subsequent cooling for the ordered phases to nucleate and grow, therefore achieving a high degree of order in the 1m/s samples. An attempt has been made to annealing the 1m/s to increase the ordering degree, however, the temperature is either too high that results in the formation of single large grain throughout the sample which is not suitable for this technique, or too low to initiate sufficient growth of D0₃ phases.

Figure 7.6. 2D XRD ring patterns of the samples prepared at different speeds, (a) 1m/s; (b) 5m/s; (c) 10m/s; (d) 20m/s.
7.3.6. Magnetic thermogravimetric analysis (M-TGA)

Thermogravimetric analysis coupled with a pair of strong magnets is often used to characterize the thermal and magnetic behavior of materials. Figure 7.8a shows the M-TGA curves of the samples for a full heat and cool cycle. All samples lose apparent mass on heating and reach a steady state above 700°C, typical of a magnetic material undergoing a ferromagnetic to paramagnetic transition during M-TGA analysis. Heating promotes the thermal fluctuation of the atoms which works against magnetic ordering, resulting in loss in magnetic susceptibility. This is clearly shown in figure 7.8b where the magnetization drops with temperature via a VSM measurement for both the as casted and annealed samples. Since the sample is attracted by the magnets positioned below the sample, the loss in magnetization reflects in the TGA curve as loss in net mass. Depending on the net amount of magnetization compare to net initially sample mass, the relative mass as displayed in figure 7.8a can be either positive or negative. The Curie temperatures are not affected by the different degrees of cooling attained at different wheel speeds. The Curie temperature is approximately 700°C for all samples as determined by the endpoint or extrapolated onset upon heating method [244]. This Curie temperature matches the Curie temperature depicted from the Fe-Si phase diagram for 6.5% of silicon [245]. Assuming, all phases (A2, B2, D0₃) have similar Tc, all samples should possess the same compositions, i.e. Fe-6.5%Si.
This is consistent with the XRD results that all the lattices parameters for all the samples are the same.

In the M-TGA curves, there are apparent differences in the rates of the weight losses for different samples. The mass drop is greater and more gradual for samples prepared with higher wheel speeds than the samples prepared with lower wheel speeds. For the 30 m/s sample, the mass of the sample gradually decreases from ~100°C to ~600°C, then sharply decreases from 600°C to 700°C. The total relative mass loss of the 30 m/s sample reaches ~175% compared to the initial net mass. For the 1 m/s sample, the mass is nearly constant until Curie temperature is approached. The total relative mass loss of the 1 m/s sample, 30%, is much smaller than the 30 m/s sample. The gradual drop in magnetization with increasing temperature is likely due to the sample consisting of multiple phases, in this case, disordered A2, and ordered B2 and D0₃ phases. Similar phenomenon was also observed on Fe-Si of different compositions by others [246]. In Fe-6.5%Si melt-spun ribbons, D0₃ can be fully suppressed, while B2 can only be partially suppressed by wheel speeds higher than 10 m/s as reported by our earlier work [50] as well as demonstrated by the TEM diffraction pattern above in Figure 7.3. The samples melt-spun at wheel speeds of 10 m/s and above contain a mixture of disordered A2 phase and ordered B2 phase, with minimal D0₃ phase. On the contrary, the samples melt-spun at lower wheel speeds possess a higher degree of ordering as demonstrated by the rotating crystal XRD results shown in Figure 7.7, which suggests they mostly consist of B2 and D0₃ ordered phases. Therefore, the onsets of mass losses are shifting towards higher temperatures for ribbons melt-spun at lower wheel speeds due to their higher ordering degree.

The relative mass losses also show a significant difference between the samples. The relative mass loss is large for samples melt-spun at higher wheel speeds, and shifting towards lower values with decreasing wheel speeds. According to the Fe-Si phase diagram [30], for 6.5%Si, D0₃ is the stable phase below ~650°C. In addition, D0₃ nucleation and growth are reported to be responsible for high permeability [63], leading to higher flux density under a weak magnetic field. Previous results [50] show that a field of around 1 KOe is needed to saturate the samples along the sample plane direction due to the demagnetization field. In the M-TGA, the field is applied perpendicular to the sample plane, where a more significant demagnetization field is present. Therefore, the ~1 KG magnet used here is not sufficient to saturate the samples. The increase in
permeability will result in higher magnetization for the samples. The increase in magnetization is confirmed by the M-TGA curve in Figure 7.8c, which shows a continuous increase in mass during the 650°C isothermal hold. For the current M-TGA set up, higher flux density leads to higher apparent mass. Therefore, for the samples melt-spun at high wheel speeds, D03 ordering is likely taking place during the heating segment, resulting in an increase in magnetization. Conversely, the magnetization is decreasing with temperature due to the thermal fluctuation of the atoms. The net effect for the D03 ordering during heating thus displays in the TGA curve as gradual and large decrease in mass as for the 30m/s, 20m/s, 10m/s, rather than a rapid and small mass loss for that of 5m/s, 3m/s and 1m/s samples. A larger amount of ordering occurs during the heating means there is less ordered phases in the sample to start with, and the amount of mass loss, therefore, can be served as an indication of the amount of ordered phases in the samples. It should be noted that the ordering process should be dependent on the heat/cool rate of the measurement. With relative fast heat/cooling, i.e. 10°C/min used in this study, the ordering starts only at high temperatures. The relative fast heat/cool rate also resulted in small hysteresis being observed.

In addition to the higher permeability of the ordered phases as a factor contributing to the larger gain in M-TGA mass, a small difference in saturation magnetization between the ordered and disordered phases may also contribute to the change in M-TGA mass. An initial study on the saturation measurement does not reveal systematical changes in the magnetic saturation as a function of wheel speeds. VSM measurement on 30m/s melt spun sample in the as-spun state and annealed state up to 1T field showed that they have the same saturation magnetization as in figure 7.8d. While the qualitative study of the ordered phases via M-TGA is reliable, quantification of the ordered phase requires a full understanding of the magnetic structure and properties of the individual phase. Future work is planned to quantify the change in magnetization and Curie point for A2/B2/D03 phases through DFT modeling. In addition, the magnetization per unit cell for each phase will be estimated through magnetic structure refinement aided by neutron studies.
Figure 7.8. (a) Magnetic TGA curves of the samples melt-spun at different speeds; (b) Magnetic moment vs. temperature measured for 30m/s as spun sample and post-annealed 30m/s sample measured at 1T field; (c) 650°C isothermal TGA curve of the sample melt-spun at 30m/s; (d) Magnetic moment vs. applied field measured for 30m/s as spun sample and post-annealed 30m/s sample measured at 27°C.

7.4. Conclusion

The wheel speed affects the cooling rate of the melt-spun Fe-6.5%Si ribbons. As measured by thermal imaging, the cooling rates change continuously with wheel speeds, ranging from $10^4$ K/s for the sample melt-spun at 3 m/s to $10^6$ K/s for the samples melt-spun at 30 m/s. The varying cooling rate induced a varying degree of order of the Fe-6.5%Si samples, which were characterized by a number of methods including TEM, normal θ - 2θ XRD, rotating crystal transmission XRD, and magnetic thermogravimetric analyses. TEM qualitatively identified the occurrences of D0₃ when the wheel speed is reduced. However, TEM is costly and challenging to extract any quantitative information. Normal θ - 2θ XRD is useful to determine the lattice parameters of Fe-
6.5%Si and thus provide guidance on the chemical composition. However, the superlattice peaks unique to the ordered phases are not strong enough to appear on the XRD pattern. Rotating crystal transmission XRD generates sufficient signal for the superlattice peaks and is not affected by texture, therefore relative intensities can be used for quantification. The magnetic thermogravimetric analysis allows the recording of the magnetic ordering that is taking place during the heating portion of the analysis, therefore indirectly provides quantitative information about the ordering that took place during the melt spinning. The proposed rotating crystal transmission XRD and the magnetic thermogravimetric analysis are effective characterization methods to quantify the degree of order present in the melt-spun Fe-6.5%Si samples, which is beneficial for studying and monitoring the ordering phenomenon in Fe-6.5%Si.
CHAPTER 8 CONSTRUCTION OF THE TIME, TEMPERATURE, AND PHASE TRANSITION CURVE OF RAPIDLY QUENCHED AND ANNEALED Fe-6.5wt%Si ALLOY

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Abstract

Process governs the structure of a material, which in turn governs the properties of the material. The processing-structure-property relationship provides the guiding principles for materials research and manufacturing. It represents the core of materials science and engineering. This work utilizes a variety of techniques to identify the critical processing parameters necessary to achieve the desired microstructure in Fe-6.5wt%Si determined in Chapter 3 and 4. The combination of the critical cooling rate derived using thermal imaging technique and the crystal structures and phases information obtained using XRD reveal the relative quantities of A2, B2 and D03 present in the Fe-6.5wt%Si samples. The result leads to the creation of a time temperature transformation (TTT) curve for the Fe-6.5wt%Si alloy system that can be used to predict and design heat treatments necessary to achieve a final microstructure.

8.1. Introduction

Fe-6.5wt%Si is a superior soft magnetic material to the current commercial favorite electric steel. The difference between the two is the addition of 3% more silicon, but this addition comes at a great cost to workability.⁵⁰, ²³⁶, ²⁴⁹ While traditional electric steels are ductile at room temperatures, extra silicon causes a hard and brittle phase to form, effectively ruining the workability. This can be avoided by changing how the material is processed to improve workability. The fundamental understanding of how a material will respond to heat treatment processes is the most important prerequisite when designing with new materials.
The relationship among the structure, properties, processing provides guidance for preparing the materials for their applications. One of the most useful tools in describing this relationship is the time-temperature-transformation (TTT) curve. This curve visualizes the processing conditions necessary to obtain desired phases. While a simple phase diagram will give the equilibrium phases present at a given temperature and composition, a TTT curve will allow for the determination of the amount of phases present during non-equilibrium conditions. If a metastable phase can be trapped at low temperatures a TTT curve will show what thermal processing conditions need to be met in order to accomplish that. Heavily studied materials like carbon steel have such a long history that their TTT curves are well mapped and used every day in industry to control the final microstructure of a wide variety of end products. However, a detailed TTT curve does not exist for every material either due to lack of study or difficulty in determining what processing conditions actually effect the final microstructure. This work looks to develop a TTT curve for Fe-6.5wt%Si using a variety of techniques, from melt-spinning and annealing processes to X-ray diffraction and Synchrotron experiments.

Previous work has shown that the critical cooling rate necessary to bypass the brittle phase is greater than 162,000 K/s and was achieved using a melt-spinning process and a wheel speed of >7 m/s. The results of that work are shown below. At greater speeds the material appears to be ductile most likely due to the suppression of the B2/D03 phase. The next step towards generating a TTT curve is apply a series of heat treatments and record the evolution of the microstructure.
8.2. Methods

Generating a fully developed TTT curve requires two parts: a cooling rate analysis and an annealing process. The two methods described here were used to complete both of these halves. The cooling rate analysis was explored using a FLIR thermal camera and a melt-spinning chamber, by varying the speed of the melt-spinning wheel multiple cooling rates were achieved. This is discussed in detail in the previous chapter where a thorough analysis of wheel speeds and their corresponding cooling rates are calculated for the Fe-6.5wt%Si system. The annealing study will be conducted using a sample of 30 m/s melt-spun ribbon. These samples will be subjected to a range of temperatures (300 – 900 °C) for varying lengths of time (1-360 minutes).

Once completed, a way to determine the corresponding microstructure was needed to continue developing the TTT curve. The microstructure for the cooling rate data has been determined in the previous paper Determining B2-D03 ordering in a Fe-6.5wt%Si Alloy. Using the data presented in that paper the top portion of the TTT curve can be generated as the critical cooling rate to trap the metastable phase (A2) is approximately 300,000 K/s. Determining the crystal structure and presence of B2 and D03 was done using a single crystal x-ray diffractometer with a 2D detector.
By comparing the ratio of the largest index peak to those corresponding to the phases of B2 and D0₃ a TTT curve can be generated.

The phase fractions of each annealed sample with measureable B2/D0₃ were plotted and according to the annealing temperature a line was fit to each one. Once fit the time necessary to achieve a 10 %, 50 %, and 90 % phase fraction of possible B2/D0₃ was predicted. These times were then used to construct a banded region of specific heat treatments for achieving specific microstructures.

8.3. Results

Figure 8.2: Laue Diffraction Patters showing 30 m/s (left) and 7 m/s (right) and the suppression of the B2/D0₃ 100 diffraction ring at high wheel speeds. Black arrows showing the (110) diffraction; white arrow showing (100) diffraction.
Figure 8.3: Relative phase fractions of B2/D03 present at various times and temperatures. (Squares 600 °C, Diamonds 700 °C, Circles 800 °C, Triangle 900 °C).

Figure 8.4: TTT annealing curves for Fe-6.5wt%Si showing 10%, 50%, and 90% (left to right) B2/D03 phase fractions. Diamond point represents the condition necessary for a crispy stamp of 45 µm ribbon into motor laminate.
8.4. Discussion

The 2D Laue patterns collected show a correlation between the wheel speed and the formation of a B2/D03 phase as indicated by the clearly defined (100) band shown in the 7 m/s sample as shown in Figure 8.2. The faster wheel speed of 30 m/s does not appear to contain this band though it is more difficult to see given the intensity of the background present in the region. Further inspection after integrating over the entire pattern revealed almost no signal being generated at that point in the diffraction pattern. This is consistent with work done previously in this area by Dr. Ouyang.3

Examining the phase fractions of the B2/D03 phases presented in the annealed ribbon, a pattern emerges for each temperature. At any given temperature there is a power law relationship between the amount of time spent on annealing and the final phase fraction of material present. This makes sense because the disordered phase of the melt-spun ribbon is a metastable phase. Once the initial energy necessary to order the atoms is achieved, the formation of B2/D03 is initially very fast, but eventually slows until the maximum amount of B2/D03 possible is formed. The scale for transformation in this study is scaled to the strongest and weakest (100)/(110) peak intensity ratio. This is due to the inability to determine exact phase composition of B2/D03 given the overlapping nature of their diffraction patterns. After plotting these phase fractions vs the time necessary to achieve them, a curve can be fit to each set which will be used to interpolate, and to a minor extent, extrapolate the necessary time needed to achieve a specific phase fraction.

Finally, by using the previous set of power law relationships it was possible to predict the necessary amount of time to achieve a phase fraction of 10%, 50%, and 90% B2/D03 given a starting randomized microstructure. There is also opportunity to predict continued growth of a sample that contains a predetermined amount of B2/D03 by using TTT curve presented.

8.5. Conclusions

Utilizing the process of melt-spinning to rapidly solidify a ribbon of Fe-6.5wt%Si, it is possible to bypass the room temperature brittle phase. Then using a single crystal x-ray diffractometer with a 2D detector, the faint signals from the brittle phases can be analyzed in order to determine the amount of B2/D03 present after cooling. This leads to the first half of a TTT Curve construction where cooling rate can be linked directly to the microstructure. Then by preforming annealing on
a fully disordered samples, a correlation between specific heat treatments and the resultant microstructure was achieved.
CHAPTER 9 GENERAL CONCLUSIONS

The story of how Fe-6.5wt%Si became a primary candidate for the soft magnetic material of choice for high efficiency applications is well-studied. However, while its discovery dates back to the early 1900’s the details of its structure, processing, properties relationship was incomplete with only extreme cases being well defined. This work has been aimed at linking each of these together to form a complete picture, where the path from a desired microstructure or material property can be followed to an end product that meets expectations. The largest difficulty in this endeavor was to link the properties being observed with a specific crystal structure present. Second to that was identifying what processing conditions would yield those specific crystal structures. While previous works were concerned with edge case scenarios of rapidly quenching using various techniques to bypass brittle phases, their effort was to explore processing methods that may solve a mechanical property issue not define the effects of processing conditions. Their results often reporting that the benefit to material properties were outweighed by increased cost of production thus halting further research fine tuning the processing conditions. Previous endeavors to link the processing conditions to a given microstructure were also hampered due to the difficulty in differentiating the phases present due to all three sharing the characteristic BCC peaks. Their strong intensities combined with much weaker superlattice peaks of the ordered phases made quantitatively determining their composition almost impossible. Not to mention the previously most effective techniques for identifying the presence of these ordered phases were costly and time consuming. The discovery of a new method for detecting and interpreting the superlattice peaks was essential in constructing a map of the TTT curve. Once implemented with the previous studies on processing parameters and material properties the full scope of what is possible with Fe-6.5wt%Si is now open for exploration. Process independent variables such as cooling rate and annealing temperature can now targeted to draw out the materials full potential. This road map will serve as a guide to future research and industrial designs opening up the way for Fe-6.5wt%Si to be utilized as never before.
REFERENCES


[247] Macziewski, Chad, Brandt Jensen, Gaoyuan, Ouyang, and Jun Cui. “In-situ cooling rate analysis of melt-spun Fe-6.5wt%Si using thermal imaging techniques.”
[248] Ouyang, Gaoyuan, Brandt Jensen, Chad R. Macziewski, Tao Ma, Fangqiang Meng, Qishen Lin, Lin Zhou, Matt Kramer and Jun Cui. “Determining Ordering in and Fe-6.5% Si Alloy.”