DEVELOPMENT OF HIGH SATURATION INDUCTION FE-NI BASED METAL AMORPHOUS ANOCOMPOSITE BY OPTIMIZATION OF GLASS FORMING ABILITY

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1. Introduction

This thesis is entitled "**Development of High B**_s**Fe-Ni Based Metal Amorphous Nanocomposite by Optimization of Glass Forming Ability**" In this Introduction section I lay out the thesis content in the context of the materials paradigm followed by the current technological and scientific motivation for the work. This is followed by a historical introduction to Metal Amorphous Nanocomposite (MANC) materials and a discussion of the Fe-Ni phase diagram which provides the thermodynamic basis for the choice of Fe-Ni-based MANCS as the subject of this thesis research. Finally, an introduction to the synthesis methods for MANC materials is presented.

1.1.Materials Paradigm

The materials paradigm is represented as a tetrahedron with synthesis, structure, properties, and performance vertices with information from each providing feedback to materials development efforts (Fig. 1.1).



Figure 1.1. The materials science tetrahedron. Redrawn from [2]

In this thesis, the processing step includes production of amorphous metal ribbon (AMR) by planar flow casting (PFC), and annealing to induce partial nanocrystallization. The latter is inclusive of annealing under stress or while rolling to introduce anisotropy and/or further thin the ribbons. Structure refers to XRD measurements and TEM imaging, which were used in this thesis to determine phases present and the size distribution of the nanocrystalline grains. Properties include glass forming ability (GFA), Curie temperature (T_c), saturation induction (B_s), magnetostriction, and formability, which were determined for the materials produced. GFA which is defined as the minimum cooling rate necessary to form an amorphous structure, can be considered an intrinsic property, since it does not depend on structure, while magnetic properties are structure dependent, and hence extrinsic. Performance reflects optimization of magnetic losses, including hysteretic and eddy current power losses. Losses in the material limit possible size reduction in components, since they lead to excess heat that must be dissipated through the surface [18].

1.2. Motivation

The International Energy Agency estimates that electric motors to account for ~46% of global electricity consumption (Fig. 1.2), resulting in 6040 MT of CO₂ emissions [3], making increased efficiency a top concern. Magnetic core losses (iron losses), including eddy current and hysteretic loss, are a significant [19] part of overall motor losses accounting for about 1-7% of the total power consumption. Reducing losses is important for efficiency improvement in electric motors. Electric motors are increasingly used in transportation, as electric vehicle adoption increases at an accelerating pace [20].



Figure 1.2. World electrical consumption by application. [3]

In light of this, the US DOE EERE Advanced Manufacturing Office (AMO) has recently funded Carnegie Mellon University to create a 2.5 kW flux-switching motor as demonstration of the use of MANC materials in high-speed high frequency motors. The motor design has a mechanical rotation speed of 5000 rpm and an electrical switching frequency of 5 kHz. This project supports the Next Generation Electrical Machinery (NGEM) program which seeks out technology relevant to large-scale industrial motors with higher power densities and efficiencies. CMU's effort has resulted in a successful prototype based on an Fe-Ni MANC material, and has demonstrated novel manufacturing processes for commercial scale manufacturing. [21] The US DOE EERE Vehicle Technology Office (VTO) has further provided funding to CMU for demonstration of a MANC based motor with a power rating of 20 kw, which will simulate future high efficiency, high power density motors for use in electric vehicles.

In motors for electric vehicles, increasing rotational speed increases power density since power $P=T \ge \omega$, (T is torque and ω is angular velocity). High motor speed, achieved by high switching frequency, can result in significant motor size and weight reduction [16]. Materials such as Si-steel are limited to several hundred Hz, while amorphous [22] and metal amorphous nanocomposite (MANC) [16,21,23] alloys are used in motors with several kHz switching frequencies, due to their much lower losses. The core loss of a magnetic material can be modeled as the Steinmetz equation:

$$P_L = k f^{\alpha} B^{\beta} = A_{Hyst} f \text{ (hysteresis)} + \frac{d^2 B^2 f^2}{\rho} \text{ (eddy current)} + \frac{d f^x}{\rho} \text{ (anomalous)}$$
 [Eq. 1.1]

where P_L is core loss; k, α , and β are fitting parameters [5,24]. $A_{(Hyst)}$ is the area of the B-H loop, d is material thickness, and ρ is electrical resistivity. Hysteresis loss increases linearly with frequency. Classical eddy current loss scales as the square of the frequency, demonstrating the importance of high resistivity and low thickness for high frequency applications. Future work will explore thickness reduction by rolling and casting thinner ribbon, as well as alloying additions to increase resistivity [25], with the aim of allowing reduced motor size by lowering thermal dissipation.

1.3. Fundamentals of magnetism

Magnetism in materials arises from the presence of dipole moments. Dipole moments result from the orbit of the electron about the nucleus, or from the inherent angular momentum known as spin. This angular momentum is quantized in units of $\hbar=h/2\pi=1.05\times10^{-34}$ J*s. The magnetic moment of electrons is typically given in units of the Bohr Magneton:

$$\mu_B = \frac{e\hbar}{2m}$$
[Eq. 1.2] [5]

where e is electron charge and m is electron mass. In SI units, the Bohr Magneton has a value of 9.274×10^{-24} J/T. The total magnetization of a material is given by:

$$M = \frac{\Sigma_{atom} x \,\mu_{atom}}{V}$$
[Eq. 1.3] [5]

The response of a material to an applied field is given by the relation magnetic induction, B and magnetic field, H. In a vacuum, this is given by:

$$B = \mu_0 H$$
 [Eq. 1.4] [5]

where μ_0 is permeability of free space, or $4\pi x 10^{-7}$ H/m. When a magnetic material is subjected to the field, induction is given by:

$$B = \mu_0(H + M)$$
 or $B = \mu_0(1 + \chi_m)H$ [Eq. 1.5] [5]

where χ_m is called the magnetic susceptibility. The intrinsic material property know as relative permeability can be defined as:

$$\mu_r = \mu_0 (1 + \chi_m)$$
 [Eq. 1.6] [5]

In a material, magnetic dipoles arrange in either a fully disordered arrangement (paramagnetic), or one of several ordered states, including ferromagnetism, ferrimagnetism, and antiferromagnetism. The materials presented in this work are ferromagnetic in their useful state. Transition from an ordered to disordered magnetic state is a second order phase transition and can be described by Landau theory. Here, free energy can be expressed by:

$$G = G_0 + \frac{a}{2}m^2 + \frac{b}{4}m^4 \dots$$
 [Eq. 1.7] [5]

where m is the order parameter. The order parameter reaches its highest value at T=0 K and goes to 0 at the Curie temperature (T_c). Due to the continuous change in order parameter, the Curie temperature is a higher order phase transformation. The material is paramagnetic when a>0 and ferromagnetic when a<0. Gibbs free energy curves and a M vs. T curve showing Curie temperature are shown in Fig. 1.3. [4]



Figure 1.3. (a) Gibbs free energy change with values of a. Material is paramagnetic when a>0, ferromagnetic when a<0. (b) Order parameter m vs. temperature, showing the Curie temperature. Redrawn from [4].

A ferromagnetic material can be classified as hard or soft. Hard and soft are distinguished by the magnitude of the coercivity (H_c) or the field necessary to demagnetize the material after it is saturated. A hard magnet will have a large value of H_c , while that of a soft magnet will be low. When a magnetic material is saturated in opposite directions, then back to the original orientation, a magnetization vs. field (M-H) loop can be traced. Magnetization in an ideal soft magnetic material is fully reversible, while in real soft and especially hard materials, a hysteresis will be seen. The area inside to loop determines the losses in one magnetization reversal cycle. Hard magnets will usually also have a substantial remanence (M_r), which is the remaining magnetization when an external field is removed. An ideal soft and hard magnetic M-H loop are shown in Fig. 1.4. [4]



Figure 1.4. (a) M-H loop of ideal soft magnetic material. (b) M-H loop of hard magnetic material showing H_c and the M_r . Redrawn from [4]

Magnetic anisotropy refers to the directional dependence of magnetic properties. Magnetic anisotropy consists of: (1) magnetocrystalline anisotropy; (2) magnetostatic (shape) anisotropy; (3) magnetoelastic anisotropy (magnetostriction); (4) induced anisotropy. [5] Magnetocrystalline

anisotropy is the only one of these that is intrinsic. In cubic materials, magnetocrystalline anisotropy takes the form:

$$E_{A} = K_{1} \left(\alpha_{1}^{2} \alpha_{2}^{2} + \alpha_{2}^{2} \alpha_{3}^{2} + \alpha_{3}^{2} \alpha_{1}^{2} \right) + K_{2} \left(\alpha_{1}^{2} \alpha_{2}^{2} \alpha_{3}^{2} \right)$$
[Eq. 1.8] [5]

Where α_1 is the direction cosine of angle between the magnetization vector, M, and the crystallographic [100] axis; α_2 the direction cosine between M and the [010] axis α_3 the direction cosine between M and the [001] axis. K₁ is the 1st order anisotropy constant and K₂ is the 2nd order anisotropy constant. If K₂ is 0 and K₁ <0, the easy axis will be parallel to the <100> directions, while if K₂ is 0 and K₁ >0, the easy axis will be in the <111> directions. [5]

Shape anisotropy occurs when a particle or magnetic phase within a material is not spherical, causing the demagnetization field to be different in different directions. This results in an easy axis along the longer axis. Induced anisotropy occurs as the result of various structural changes occurring during materials processing. Magnetoelastic anisotropy occurs due to the interaction of mechanical stress and magnetostriction properties. An applied stress will result in an easy axis forming either parallel or perpendicular to the stress direction. [5]

In a soft magnetic material, H_c should be as small as possible. We can define an anisotropy field, which is the field necessary to saturate the material along the hard axis:

$$H_k = \frac{2K_1}{M_s}$$
 [Eq. 1.9] [5]

Where M_s is saturation induction. The anisotropy field form the upper bound for coercivity, so reducing anisotropy can lower H_c . Efforts to reduce coercivity have historically trended towards the development of coarse-grained materials, to increase domain wall mobility by reducing pinning from grain boundaries. Magnetocrystalline anisotropy is intrinsic, so it cannot be reduced by processing. However, if the grain size is significantly reduced below the magnetic exchange length, then a large number of grains of random orientation will be present in a single exchange volume, which leads to averaging out their magnetocrystalline anisotropy. This is known as the random anisotropy model. [26,27] Anisotropy then becomes:

$$\langle K \rangle = \frac{K_1^4}{A^3} D^6$$
 [Eq. 1.10] [28]

where D is grain size and A^3 is exchange stiffness. Since coercivity is proportional to anisotropy, this D⁶ dependence on grain size allows dramatic reduction in coercivity with grain size reduction below exchange length, as seen in the curve in Fig. 1.5, and is one of the main mechanisms allowing excellent magnetic softness in MANC materials. The random anisotropy model is only applicable when the grains are exchange coupled, so the Curie temperature of the amorphous phase in these materials must be above the operating temperature.



Figure 1.5. Herzer curve, showing dependence of coercivity on grain size. Redrawn from [4]

1.4. History of MANC materials

The first MANC material was FINEMET, developed by Yoshizawa et al [29] in 1988. This was an Fe based material, with B-Si-Nb glass formers and 1% Cu added as a nucleation agent. This alloy had extremely soft magnetic properties, but induction was fairly low, at 1.4 T. Attempts to improve the saturation induction led to the development of NANOPERM in 1992 [30]. Despite their excellent magnetic softness, the Fe based MANCs suffer from poor mechanical properties, namely extreme brittleness [31], which makes them unsuitable for motor applications. Additionally, the amorphous phase in NANOPERM alloys has a very low Curie temperature, limiting maximum operating temperature. [32] The next alloy to be developed was HITPERM in 2002, based on Fe and Co in ratios similar to bulk crystalline Hiperco alloys [33]. These alloys

have high saturation inductions, but their high magnetostrictive coefficients result in higher losses, making them unsuitable for higher frequency applications. Co-rich alloys were developed most recently, with Co-Fe ratios selected for near-zero magnetostriction. [34] These alloys have very low losses and can have their permeability tuned over 4 orders of magnitude by applying stress during crystallization [35–37]. Unfortunately, induction is limited to ~1 T, limiting their uses in motor applications. Aronhime et al [24,38] most recently developed Fe-Ni based MANC alloys, which combine excellent magnetic softness, good mechanical properties, and moderately high saturation induction of ~1.2 T. These alloys have already been demonstrated in a prototype motor [21], but the saturation induction would need to be further increased for optimized motor designs. A comparison of commercially available and well-developed experimental alloys is shown in Fig. 1.6.



Figure 1.6. Comparison of some magnetic properties of existing MANC materials. [5]



1.5. Alloy Composition Selection and the Fe-Ni Phase Diagram

Figure 1.7. The Fe-Ni phase diagram. [6] (b) Detailed expansion of the Fe-Ni phase diagram at low temperatures. Redrawn by M. E. McHenry from [7].

The Fe-Ni systems is the next logical choice to explore for MANC alloy development. The Fe-Ni phase diagram is shown in Fig. 1.7a. A small δ (BCC) region exists at the highest temperatures, and Fe compositions up to x=0.04. For the majority of compositions and temperature range, the structure is a disordered γ (FCC) phase. At lower temperatures, this transforms to the α phase in Fe-rich compositions, which is again BCC. A eutectoid transformation occurs at 353 °C and 50 at.% Ni, as γ transforms to α and the ordered FeNi₃ phase. [39,40] The curved dashed line shows the Curie temperature of the γ phase, while the small horizontal dashed line at the Fe-rich side of the diagram shows the Curie temperature of the α phase.

The low temperature region of the Fe-Ni phase diagram has been more recently explored. Yang and Williams [7] proposed several changes base on previous work, including a monotectoid reaction, $\gamma_2 \rightarrow \gamma_1 + \alpha$, in the temperature range between 400 and 450 °C, where γ_1 is paramagnetic FCC austenite, α is BCC ferrite, and γ_2 is ferromagnetic FCC austenite [41]. The temperature of the monotectoid is generally accepted as 400 °C, based on a calculated phase diagram by Chuang et al. [42] At lower temperatures miscibility gap has been shown to occur ($\gamma_1+\gamma_2$), based on the calculations of Chuang et al [42] and expanded by Yang and Williams [7]. This is shown as dashed lines in Fig. 1.7b, while the spinodal boundaries are shown as cross-hatched lines. Yang and Williams also experimentally confirmed the stability of the γ " phase, shown in Fig 1.7b [7].

The miscibility gap forms due to magnetic terms of the free energy, as magnetic ordering results in different free energy that of the paramagnetic phase. This results in the magnetic phase becoming unstable, causing phase separation into 2 phases with the same crystal structure but different composition. 1 of the phases becomes paramagnetic after becoming chemically enriched in the non-magnetic component. The resulting miscibility gap ends in a tricritical point, occurring at ~450 °C and 50 wt% Ni in Fig. 1.7b. [43]

Based on the work of Aronhime et al [24,38] and Ipus et al, [44] an alloy with magnetic elements in a Fe-70%-Ni-30% ratio is chosen as a starting point. This composition of magnetic elements was chosen due to its optimal combination of high saturation induction, low coercivity, and avoidance of the hard magnetic FeNi₃ phase seen in more Fe-rich compositions. Additionally, annealing takes place in the 2 phase BCC+FCC region of the phase diagram, and these phases are therefore seen in the annealed state. [45] This Fe-Ni ratio has also been found to have the highest magnetic moment in the γ phase [46], and is thus the basis for all Fe-Ni alloys developed by the group.

$$\begin{bmatrix} Fe \\ Ni \\ Co \end{bmatrix} + \begin{bmatrix} B & C \\ Si & P \\ Ga & Ge \end{bmatrix} + \begin{bmatrix} Ti & V & Cr \\ Zr & Nb & Mo \\ Hf & Ta & W \end{bmatrix} + \begin{bmatrix} Cu \\ Ag \\ Au \end{bmatrix}$$
1. Magnetic 2. Glass Formers 3. Glass Formers+ 4. Nucleation Elements Growth Inhibitors Agents

Figure 1.8. The 4 groups of elements that form a typical MANC alloy. [8]

Fig. 1.8 shows the typical elements used in MANC alloys and their functions. Matrix 1 is the magnetic elements. Matrices 2 and 3 are the glass formers, which are added to allow the material to be quenched into an amorphous state. Elements in matrix 3 also act as growth inhibitors, preventing excessive grain growth. The elements in matrices 3 and 4 also affect activation energy for primary crystallization (E_a), which determines the amorphous material's stability against crystallization. [47,48] The effects of the alloying elements on activation energy will be further discussed in Section. 7.3. Matrix 4 consists of nucleation agents, which help achieve a fine grain structure by increasing nucleation density. In Fe-Ni alloys, nucleation agents were found to be of no benefit and are excluded. As will be discussed further in Ch. 3, a large difference in atomic size

is beneficial to GFA. A growth inhibitor element with larger atomic size is also more effective at slowing growth. [5] B was chosen as a glass former due to its small atomic radius [49] and formation of a deep eutectic with the Fe-Ni composition of this alloy (see Fig. 3.4). Si is chosen as it increases the viscosity of the melt. For the growth inhibitor, the optimal element is Zr, due to its large atomic radius. [49] However, the extreme reactivity of Zr makes it difficult to process, so Nb was substituted. The composition space for this work is thus chosen to be $(Fe_{70}Ni_{30})_{100-x}(B-Si-Nb)_x$.

Some alloys use nucleation agents (matrix 4) to increase nucleation density and thus reduce grain size. Cu forms very fine clusters around 5 nm in diameter at temperatures below T_x [48,50], which form heterogeneous nucleation sites for nanocrystals [51]. The (111) planes of FCC Cu form low energy interfaces with (011) BCC Fe planes, in the case of Fe alloys, encouraging nucleation [52]. Another explanation is that the precipitation of Cu clusters expels Fe into the remaining amorphous matrix, enriching the space between clusters with Fe, which encourages nucleation [53]. Many non-Fe-based alloys neither require Cu for fine grain structure, nor benefit from it. This is believed to be due to the fact that certain magnetic elements, such as Co, have lower driving force for phase separation and prevent Cu clustering [54]. A summary of the effects of alloying elements is given in Lashgari et al [52].

1.6. Synthesis Methods for MANC Material



Fig. 1.9. (a) Slotted crucible used in *planar flow casting*; (b) cartoon showing melt pool in implementation of *planar flow casting*. [9]

Synthesis of MANCs requires the production of an amorphous precursor material. The most common method of producing amorphous material for MANCs is by planar flow casting (PFC), shown in Fig. 1.9a [9]. A crucible with a nozzle is positioned over a rotating Cu wheel. The crucible is pressurized to eject the molten metal onto the wheel, resulting in a 15-35 μ m continuous ribbon, which is subject to a cooling rate of up to 10⁶ K/s. The main feature that distinguishes PFC from the earlier process known as melt spinning is that the nozzle is positioned close enough to constrain the melt puddle, which results in better control and allows casting of significantly wider ribbons. Many parameters, including the physical dimensions of the components, the ejection pressure, and wheel speed interact to control ribbon quality and cooling rate (Fig 1.9b).

The main parameters that determine ribbon dimensions and the success of the cast are crucible pressure, gap size, and wheel speed. These 3 form an operating window in which a cast can be successful. If the wheel speed is excessive, an inertial limit is reached, and the ribbon cannot wet

the wheel fast enough. If the pressure is excessive, the puddle will balloon beyond the nozzle slot width, resulting in uneven ribbon. [55] The effect of these parameters on ribbon thickness are given by:

$$d = K \frac{a_n}{v} \sqrt{\frac{2p}{\rho}}$$
[Eq. 1.11] [56]

Where d is ribbon thickness, K is a proportionality constant, a_n is nozzle width, p is pressure, v is wheel velocity, and ρ is alloy density. Thickness increases with pressure as $(p)^{0.5}$, but paradoxically, cooling rate increases as well, up to a maximum, then decreases with higher p. the reason for this is improved wetting and ribbon adhesion at higher ejection pressures. [57] With other parameters, cooling rate is proportional to d.

Defects in the ribbon, in the form of thickness nonuniformity, arise either from wheel defects, or instabilities in the molten puddle. The first of these are known as template transfer defects, [58] and are caused primarily by surface roughness on the wheel, but also by out-of-roundness or thermal expansion. [59] The periodicity of these defects does not change with wheel speed. The second type, known as pulse transfer defects, result from instability in the melt puddle and air entrapment. They may be reduced by optimizing wheel speed, pressure and gap size. [58]

1.7. Thesis structure

In the remainder of this document, I will present my hypotheses, and show how work done supports my conclusions. In Section 3, I will present theories of GFA, and describe a method I developed for ranking GFA in ternary composition ranges, as well as the experimental verification. In section 4, I will show how this method was applied to develop new alloys with higher magnetic element content. annealing treatments, structural studies, and resulting magnetic properties are presented. In section 4, I will compare newly developed alloys vs. state-of-the art commercial magnetic alloys and measure their magnetic properties. In section 5, I will present the results of alloying additions

to increase formability temperature range and simplify thermomechanical forming. Finally, I will summarize remaining future work in section 6.

2. Hypothesis

The goal of this work is to develop a method to optimize GFA, and to use this method to develop alloys with lower glass former content and better magnetic properties, without compromising GFA. I will demonstrate:

- 1. Thermo-Calc modeling can be applied to soft magnetic amorphous alloy systems to identify compositions that have minima in either liquidus temperature or solidification range, and that these compositions will have good glass forming ability (GFA). [60]
- 2. Using Thermo-Calc simulations, we can identify compositions with good GFA with lower percentage of glass formers, and hence higher magnetic element content, to increase saturation induction, B_s.
- 3. These optimized alloys will have saturation inductions, Curie temperatures, and coercivities that compare favorably with state-of-the-art commercial alloys. Losses at AC frequencies, up to several kHz, will compare favorably with these alloys.
- 4. The optimized alloys can be successfully cast on a commercial scale.
- 5. Additions of small amounts of an additional transition metal (TM) can be used to increase the temperature difference between T_c and T_x , known as ΔT_{xg} , which will increase the temperature range in which the material can be thermomechanically processed, which is necessary for motor applications.
- 6. JMAK kinetics of primary crystallization can be determined using vibrating sample magnetotometry, by performing isothermal measurements and measuring magnetization vs. time. In these alloys, crystallization occurs above the Curie temperature of the amorphous phase, so any magnetization measured will be due to crystallization.

3. Optimization of Glass Forming Ability

3.1. Structure of the Amorphous State

Early on, metallic glasses were thought to consist of completely random atomic arrangements. Later models included Bernal's dense random packing (DRP) model [61,62]. Bernal noted, in hard sphere packing, that spheres would form clusters consisting of one of 5 types of polyhedra, centered on an atom of another size. (Fig. 3.1a) [10]. Another atomic species of a different size will fill the spaces between clusters. This short-range order (SRO) further stabilizes the liquid phase and introduces a free-energy barrier to crystal nucleation, since crystal nucleation will disrupt existing ordering. This model, however, underestimates density of real metallic glass. Several studies have suggested the presence of icosahedral clusters as a basic component of the amorphous structure [63-66]. Miracle [10,11,67] later considered icosahedral atomic clusters centered on an atom of a different size. The clusters are then arranged on a close-packed lattice. The clusters have no specific rotational orientation with respect to each other, and hence longrange order is absent. This type of medium-range ordering (MRO) is shown in Fig. 3.1b. Clustering persists for ~1 nm, and then breaks down. Sheng [68] proposed a similar model, with polyhedral clusters of metal atoms arranged in icosahedral, rather than an HCP or FCC arrangement. Cheng and Ma [69] note that the exact order may actually be a mixture of the two, with exact proportions of each depending on the alloy composition.



Fig. 3.1. (a) The five Bernal polyhedral and holes. [10] (b) An example of medium range order (MRO) in a multicomponent metallic glass. [11]

Soklaski et al [70] studied Cu-Zr binary alloys, and noted that an increasing density of Cu-centered icosahedra was present in the structure with cooling, with the formation of interconnected icosahedral networks appearing near the glass transition temperature. Another study suggested that the formation of a continuous backbone of interconnected icosahedral clusters leads to the changes seen in glass transition, and that outside the backbone structure, truly amorphous regions are present. [71] Higher levels of interconnectedness have been correlated with higher Young's modulus. [72]

3.2. Magnetic Optimization

The goal of improving GFA in soft magnetic alloys differs from that of bulk metallic glass (BMG). Unlike in BMGs, the thickness of the amorphous section does not need to be increased, since it is advantageous to have thin sections for laminations. However, increased GFA would allow the glass former concentration to be reduced, improving magnetic properties. It was recognized that significant improvements in B_s can be achieved by increasing the magnetic element content, which led to the development of NANOPERM by Suzuki et al [30]. Since then, several studies have

found significant improvements in B_s in Fe-based amorphous/nanocrystalline alloys by increasing magnetic element content [73–78]. However, this comes at the expense of glass forming elements, which can reduce GFA. The studies either ignored GFA or determined it by trial and error.

In addition to two metalloid or nonmetallic elements, MANC materials typically contain a transition metal with a large atomic size. This element increases atomic size mismatch, promoting GFA. In addition, when primary crystallization begins, the low solubility of this element in the crystalline phase results in it being ejected to the residual amorphous matrix. The increased concentration of these elements stabilizes the residual amorphous matrix, limiting crystal growth. Therefore, these elements are known as growth inhibitors [5]. The addition of transition metals has a significant deleterious effect, in that it reduces B_s of the alloy. Therefore, the need for growth inhibition and GFA must be balanced against B_s , and the minimum of these additions should be used [75].

Crystallization in MANCs can follow one of three paths. First, a 2-step process most commonly seen, where primary crystallization occurs and then is inhibited by enrichment of the residual amorphous matrix. At higher temperature, the amorphous matrix crystallizes in the secondary crystallization process. Second, if the composition of the amorphous precursor is close to that of the equilibrium crystalline products, the material will crystallize by polymorphic crystallization, which occurs in one step, without long-range diffusion. A third possibility is eutectoid crystallization, where the alloying elements partition into 2 distinct regions that then crystallize into different phases. A 2-step process is preferred for MANCs, since it allows the formation of very fine crystals surrounded by a residual amorphous matrix [5].

3.3. Fragility, Kauzmann's Paradox, and the Nature of the Glass Transition

The fragility of a liquid (Angell [12,79,80]) is described by the change in the liquid's properties with temperature as it cools to T_g . A liquid that shows Arrhenius behavior is defined as strong, becoming increasingly fragile with greater deviation [81,82]. Debendetti and Stilligner [83] have noted that a fragile liquid will have many local minima in energy of atomic structure, while strong liquids tend to only have one major minimum, in addition to the crystalline minimum. Strong liquids tend to be more likely to avoid crystallization, since they have greater viscosity near T_g , slowing diffusion and increasing GFA.

A glass transition in amorphous materials is from a hard, brittle "glass" to a viscous "supercooled liquid." The glass transition temperature (T_g) is arbitrarily defined as the temperature at which the material reaches a viscosity of 10^{12} Pa*s. The "glassy" state is a metastable nonequilibrium structure. Thermodynamic consideration for the glass transition indicates that if the entropy of the supercooled liquid is extrapolated on cooling to low temperature, for many glasses it falls below the entropy of the crystalline phase, and in some cases below zero, violating the third law of thermodynamics (Fig. 3.2). The solution to this problem is to say that there is a transition, known as "glass transition," where the supercooled liquid changes into a "glass." There is a corresponding change in slope of the entropy curve, thus avoiding the paradox. The temperature [12,84], and this crossing is more likely to occur in fragile than in strong liquids [79]. The Kauzmann temperature forms the lower bound of the glass transition temperature in a material. Lu and Li [85] noted that glass transition temperature scales linearly with the average melting point of the elements, while Donald and Davies [47] noted that crystallization temperature increases with decreasing average

outer electron concentration of the constituent elements. These observations will be used to tune T_g and T_x to maximize formability.



Figure 3.2. An example entropy vs. temperature curve showing Kauzmann's paradox. Modified from [12]

3.4. GFA Criteria

The critical cooling rate (R_c) is the minimum cooling rate for which an amorphous material forms for a given composition. R_c is difficult to measure experimentally, so several criteria were proposed to measure GFA of alloys. Turnbull [86] proposed the earliest of these: the reduced glass transition temperature:

$$T_{\rm rg} = (T_{\rm g}/T_{\rm l})$$
 [Eq. 3.1] [86]

where T_g is the glass transition and T_l is the liquidus. The liquid can be expected to crystallize only below T_x , while below T_g , diffusion is no longer possible, preventing crystallization. Thus, reducing the interval between these 2 temperatures reduces opportunities for crystallization. Discrepancies between predicted and experimental GFA resulted in the developing other criteria. The most commonly used is the supercooled liquid range,

$$\Delta T_{\rm xg} = (T_{\rm x} - T_{\rm g})$$
 [Eq. 3.2] [87]

where T_x is the onset of crystallization on heating (in K) [87]. Neither criterion can predict GFA for all alloy systems, and several others have been proposed to account for these discrepancies. Guo et al [88] tested a large number of GFA criteria against all known glass-forming alloys and found that the parameter:

$$\gamma_{\rm m} = (2T_{\rm x} - T_{\rm g})/T_{\rm l}$$
 [Eq. 3.3] [88]

Predicted GFA for the widest range of alloys. These criteria will be used to rank experimental alloys and compare to predicted results, with a larger value indicating better GFA. Since crystallization occurs by a nucleation and growth process, T_x strongly depends on heating rate. Thus, the parameters above can only be used to rank GFA if all measurements are performed at the same heating rate.

3.5. Theories of GFA

Researchers designing amorphous systems have often used three empirical rules [89–91]. A system should contain:

- 1. At least 3 atomic species.
- 2. 12% or more difference in the size of the atoms.

3. Negative enthalpy of mixing of the elements in the liquid phase.

Rule 2 is the inverse of a Hume-Rothery rule for solid solubility [92]. Systems meeting these 3 requirements tend to form eutectics when solidified under equilibrium conditions, which is beneficial, as the liquid phase is stable down to lower temperatures. Additionally, the number of atomic species and the size difference was believed to result in "confusion," where the additional complexity of the alloy slowed the kinetics of crystallization. [93,94]. The complexity of the crystalline phases also makes free energy reduction from crystallization minimal. [95]. Historically, there have been attempts to provide more comprehensive and predictive theories of glass formation. The most-well studied are based on increasing the liquid phase density. [89,96]. It has been shown that alloys with the highest density in the liquid have the best GFA, since this results in in higher viscosity and less free volume in the supercooled liquid, which slows crystallization kinetics [96–99]. Chattopadhyay and Murty showed that for some alloys, the elemental viscosity of additions is a better predictor of GFA than the 3 empirical rules [100].

Jalali and Li [101,102] introduced a "packing density paradox," where the addition of alloying elements of the correct atomic sizes can result in an amorphous state with higher packing density than in the solid-solution crystalline phase. They noted, however, that this alone cannot explain GFA, as an ordered crystalline structure with a higher density is always possible, so the kinetics of crystallization are important to GFA as well. They noted that compositions with multiple competing crystalline phases had better GFA, and eutectic compositions were favored. The eutectic transformation results in two separate phases forming, which necessitates long range diffusion and results in slower kinetics. Additionally, the liquid phase is stable to lower temperatures in these compositions, resulting in lower driving force for crystallization.

A similar understanding of the role of atomic size mismatch proposed by Egami and Waseda [103,104] is known as atomic-level stresses. With the addition of alloying elements of different size, an amorphous structure can adjust its structure to minimize pressure on each individual atom, while in the equilibrium crystalline state, individual atoms will be under ever-increasing stress, and eventually the amorphous phase becomes more stable than the disordered crystalline phase. This condition give rise to a criterion for minimum concentration for a stable amorphous phase based on volume mismatch for glass formation. For a binary alloy, the minimum concentration of the second elements can be obtained from the equation:

$$x_B^{min} \left| \left(\frac{r_B}{r_A} \right)^3 - 1 \right| = 0.1$$
 [Eq. 3.4] [103]

Where x^{min}_{B} is the minimum concentration of the second atom, and r_{a} and r_{b} are the host and second atom, respectively. While models based on atomic size difference are based on the first of the Hume-Rothery rules for solid solubility, another explanation is based on differences in crystal structures of the constituent elements (2nd Hume-Rothery Rule). Based on the work of Liu on ion beam mixing, the maximum possible amorphization range (MPAR) model was developed, which correlates GFA of an alloy system with the composition range between the maximum solid solubilities in a eutectic [105,106], which is in turn dependent on the difference in the crystal structures of the alloying elements. The larger this composition range ("amorphization range"), the higher the expected GFA.

The theories mentioned above serve as guidelines for my future research, as they will allow choosing glass forming elements to maximize GFA. However, none of them allow quantitative comparison between alloys or allow identification of alloys with good GFA in ternary and higher order systems. Identifying compositions with good GFA in the 5-component alloys studied here will require methods discussed below.

3.6. Thermodynamic Approach to GFA Prediction

While models of GFA based on amorphous density can be useful for binary alloys, they rapidly become too complex for multicomponent alloy systems. Thermodynamic based modeling can allow prediction of GFA even in multicomponent alloys. An early thermodynamic model is based on the T_0 curves. The T_0 curves between the liquidus and solidus phase give the minimum undercooling necessary for the liquid to solidify without partitioning [13,107]. Where the T_0 curves extend below the glass transition temperature, the glassy phase becomes more stable than the solid-solution crystalline phase of that composition [108–110]. This allows the material to be cooled below T_g while avoiding crystallization to the solid-solution phase, which requires no long-range diffusion. An example of T_0 curves that suggest good GFA are shown in Fig. 3.3a, while those in Fig. 3.3b suggest poor GFA. However, this does not offer a way to rank or compare alloys and is of limited used beyond binary systems.


Figure 3.3. T₀ curves of an alloy with good expected GFA (a) and poor expected GFA (b). [13,14]

It has long been known that alloys with lower liquidus temperatures have higher GFA, and alloys at or near eutectic points tend to have the best GFA. Several studies have successfully used thermodynamic calculations to locate minima in liquidus temperatures for a range of compositions [111–113]. However, these calculations are complex to perform. A study by Zhang et al [114] has used Thermo-Calc software to calculate liquidus temperature for glass forming alloys over a 3 component space. An additional step was the calculation of the solidification range, which is defined as the difference between solidus and liquidus temperatures. Alloys showing a minimum in both liquidus and solidification range are expected to have good GFA.

3.7.*Thermo-Calc Modeling*

Thermo-Calc is a CALPHAD (calculation of phase diagrams) based software that is used to determine thermodynamic equilibria under given conditions using databases of thermodynamic properties. We use Thermo-Calc to simulate liquidus and solidus temperatures of a (Fe₇₀Ni₃₀)₈₀(B-Si-Nb)₂₀ composition, while varying the 3 glass forming elements (B, Si, Nb) in concentration, and to plot those temperatures on pseudo-ternary diagrams. This allows identification of minima in liquidus temperature and solidification range (difference between solidus and liquidus) as shown in Fig. 3.4. **All compositions are given in mole %.** The database used was TCFE9 (Steel and Febased alloys). This database covered the largest part of the compositions explored below, though at their highest concentrations, B and Nb were outside the optimal range for this database. To ensure accuracy, predicted and measured liquidus temperatures were compared, and found to have excellent agreement.



Figure 3.4. Pseudo-binary phase diagram of $Fe_{70}Ni_{30}vs$. B at%, defining solidus, liquidus, and solidification range, as generated by Thermo-Calc. Cementite here is Fe₃B.

Binary phase diagrams for each glass forming element with Fe exhibit eutectic compositions: 17 at% for Fe-B, 12 at% for Fe-Nb, and 33 at% for Fe-Si [115]. A pseudo-binary phase diagram of Fe-Ni vs. B was generated in my study. Thermo-Calc simulation of liquidus and solidus temperature was performed keeping the Fe to Ni ratio constant at 70% to 30% and the overall concentration of glass formers at 20%. The at. % of Nb, B, and Si were varied from 0-20%, and results plotted on a pseudo-ternary diagram. For solidification range, solidus temperatures were subtracted from liquidus and the results plotted. Results of Thermo-Calc simulations for liquidus temperature and solidification range are shown in Fig. 3.5. Fig. 3.5a shows two minima: from 12-18% B and 0-7% Si, identified as region 1 in the figure, and from 3-5% B and 1-4% Si identified

as region 4. A minimum in solidification range occurs over most of the range, with slightly higher solidification range at ~ 0.5-2% Si. An additional minimum occurs from 1-10% B and 0-12% Si, which doesn't correspond to a liquidus minimum (region 3). The 2 liquidus minima correspond to Fe-B and Fe-Nb eutectics: 20.7% B, Nb or 6.9% Nb and 20.7% B which are outside of the range examined here. Since the Fe-B eutectic results in the dominant minimum in liquidus, the pseudo binary Fe₇₀Ni₃₀-B phase diagram was generated by Thermo-Calc. The result is shown in Fig. 3.4. The eutectic point shifts to 16 at% B.



Figure 3.5. Liquidus T (a) and solidification range (b) calculation of a $(Fe_{70}Ni_{30})_{80}(B-Si-Nb)_{20}$ composition in Thermo-Calc plotted in pseudo-ternary diagrams, variying B, Si, and Nb from 0-20%. Plotted with B and Si on the axes, with the balance Nb. Compositions are marked by color indicating relative GFA, as determined by comparing T_{rg} .

3.8.X-ray Diffraction (XRD)

XRD is typically used to determine crystal structure and lattice parameter of crystalline materials. XRD works by diffraction of x-rays from crystalline planes, resulting in constructive interference when the Bragg condition: is satisfied. For amorphous materials with no LRO, the XRD pattern will consist of several very broad peaks of low intensity, which corresponds to a distribution of atomic spacings. We use XRD to determine whether a material is amorphous, since the presence of even a relatively small amount of crystallinity will result in readily apparent peaks emerging from the amorphous curve. Due to the small size of the nanocrystals, the peaks will exhibit some broadening, as given by the Scherrer equation:

$$\tau = \frac{\kappa\lambda}{\beta\cos\theta}$$
 [Eq. 3.6] [116]

Where τ is grain size, K is a constant, usually ~0.9, λ is x-ray wavelength, β is peak width at full width half max, and θ is Bragg angle. Due to the presence of the residual amorphous phase, Scherrer's equation is difficult to apply, since it is difficult to separate the broad amorphous peak from the crystalline peaks.

Region 1:

Twelve compositions within this minimum in liquidus temperature were produced. The ribbons cast successfully and passed a bend test, indicating that they were fully amorphous [117]. Solidification range also shows a minimum in this composition range, so good GFA was expected. Four compositions were produced at compositions slightly off the minimum liquidus region for comparison (region 2). These alloys were cast successfully and were fully amorphous as seen on XRD results. Previous studies showed that some compositions with good GFA may occur close to, but not always on, the minima [114].

Region 4:

Four compositions were produced. The casts all produced very short, brittle flakes. XRD results, shown in Fig. 3.6a, indicate that the material is crystalline. The XRD patterns do not match those of known Fe-B and Fe-Nb crystallization products. This composition range has a shallow minimum in liquidus, with no corresponding minimum in solidification range, which rationalizes the poor GFA.



Fig. 3.6. (a) XRD results for wheel side $(Fe_{70}Ni_{30})_{80}Nb_{15}Si_1B_4$, $(Fe_{70}Ni_{30})_{80}Nb_{14.5}Si_2B_{3.5}$, $(Fe_{70}Ni_{30})_{80}Nb_{14}Si_3B_3$, and $(Fe_{70}Ni_{30})_{80}Nb_{14.5}Si_3B_{2.5}$ alloys (region 4), with significant crystallinity and (b) wheel side XRD of the $(Fe_{70}Ni_{30})_{80}Nb_{7.5}Si_{8.5}B_4$ (top) and $(Fe_{70}Ni_{30})_{80}Nb_8Si_7B_5$ (bottom) (region 3) alloys showing surface crystallization, and an amorphous peak to remain.

Region 3:

Two compositions were produced in this range. There is a deep minimum in solidification range, but no corresponding minimum in liquidus. Melt spinning resulted in continuous ribbon, but all samples were somewhat brittle, indicating the presence of crystallization. XRD results, shown in Fig. 3.6b, all have an amorphous peak, but also a small crystalline peak at about 70° 20. The GFA was greater than the 3-5% B compositions, likely due to the deep minimum in solidification range, but less than compositions that display minima in both measurements.

3.9. Differential Scanning Calorimetry (DSC)

DSC is a technique that works by heating a sample, while keeping its temperature the same as an empty reference pan. The difference in heat flow is recorded, and can be used to determine heat capacity, as well as identify the onset of exothermic and endothermic, as well as higher order, transformations. For this study, we use DSC to determine T_g , T_x , and the liquidus temperature, which are used to quantitatively determine and rank GFA of alloys. Crystallization and melting are exothermic and endothermic, respectively, while glass transition results in a change in heat capacity seen as a decrease in slope in the DSC heat flow vs. temperature curve. Curie temperature (T_c) is determined by DSC as an increase in slope at the transition. T_c is important to identify, since it determines the maximum operating temperature of the alloy.

Fig. 3.7 shows DSC curves which exhibit the following features:

- 1. A change in slope at 405 °C
- 2. A slight change in slope before the first exothermic peak, at ~455 °C
- 3. A large exothermic peak starting at 475°C
- 4. A second large exothermic peak starting at 537 °C

Feature one was confirmed by physical properties measurement system (PPMS) measurements to be Curie temperature. Feature two was taken to be T_g , as reported in other literature on amorphous and nanocomposite soft magnetic materials [118,119]. Features three and four were primary and secondary crystallization, respectively.



Figure 3.7. Sample DSC curve (a) and its derivative (b) showing T_c , T_g , and crystallization Ts.

Table 3.1 shows results of DSC measurements. DSC curves of (Fe₇₀Ni₃₀)₈₀Nb₁₅Si₁B₄, (Fe₇₀Ni₃₀)₈₀Nb_{14.5}Si₂B_{3.5}, (Fe₇₀Ni₃₀)₈₀Nb₁₄Si₃B₃, and (Fe₇₀Ni₃₀)₈₀Nb_{14.5}Si₃B_{2.5} compositions were all featureless in terms of exothermic reactions, confirming completion of nanocrystallization.



Figure 3.8. Predicted T₁ plotted against measured T₁.

The T₁ temperatures and Thermo-Calc results show mostly good agreement, with the exception of 3 outliers at $(Fe_{70}Ni_{30})_{80}B_{15}Si_0Nb_5$, $(Fe_{70}Ni_{30})_{80}B_{14}Si_0Nb_6$, and $(Fe_{70}Ni_{30})_{80}B_{18}Si_0Nb_2$ compositions, as seen in Fig 3.8. These outliers are all high B, low Si compositions, and occur at the edges of the minimum in liquidus at region 1, indicating that the minimum is shifted to higher B concentrations. The error may be the result of limitations of the Thermo-Calc database used, as B is outside the recommended range. Nonetheless, only 1 of the compositions ((Fe₇₀Ni₃₀)₈₀B₁₈Si₀Nb₂) deviates by more than 50 °C from predictions, confirming the accuracy of these results.

Composition	Tg	Tx	Tı	Tl (predicted)	Tc
	(°C)				
$(Fe_{70}Ni_{30})_{80}B_4Si_{8.5}Nb_{7.5}$	430	430	1225	1249	302
$(Fe_{70}Ni_{30})_{80}B_5Si_7Nb_8$	458	470	1235	1248	294
$(Fe_{70}Ni_{30})_{80}B_{12}Si_3Nb_5$	453	497	1197	1205	314
$(Fe_{70}Ni_{30})_{80}B_{12.5}Si_7Nb_{0.5}$	480	480	1112	1151	413
$(Fe_{70}Ni_{30})_{80}B_{13}Si_2Nb_5$	462	475	1193	1191	318
$(Fe_{70}Ni_{30})_{80}B_{14}Si_0Nb_6$	457	470	1205	1152	307
$(Fe_{70}Ni_{30})_{80}B_{14}Si_1Nb_5$	463	498	1192	1174	341
$(Fe_{70}Ni_{30})_{80}B_{14}Si_5Nb_1$	463	485	1109	1137	415
$(Fe_{70}Ni_{30})_{80}B_{14.5}Si_4Nb_{1.5}$	457	477	1107	1146	404
$(Fe_{70}Ni_{30})_{80}B_{15}Si_0Nb_5$	450	465	1176	1129	339
$(Fe_{70}Ni_{30})_{80}B_{15}Si_1Nb_4$	451	458	1166	1157	358
$(Fe_{70}Ni_{30})_{80}B_{15}Si_3Nb_2$	457	478	1102	1149	398
$(Fe_{70}Ni_{30})_{80}B_{15.5}Si_2Nb_{2.5}$	445	471	1109	1145	393
$(Fe_{70}Ni_{30})_{80}B_{16}Si_0Nb_4$	445	461	1094	1100	370
$(Fe_{70}Ni_{30})_{80}B_{16}Si_1Nb_3$	446	467	1103	1130	392
$(Fe_{70}Ni_{30})_{80}B_{16.5}Si_{0.5}Nb_3$	448	462	1106	1132	400
$(Fe_{70}Ni_{30})_{80}B_{17}Si_0Nb_3$	452	465	1108	1134	400
$(Fe_{70}Ni_{30})_{80}B_{18}Si_0Nb_2$	455	470	1107	1181	422

Table 3.1. DSC measured T_gs, crystallization temperature, and liquidus temperature of the alloys.

The GFA parameters of the alloys were calculated (in degrees K), and the results are shown in Table 3.2. The ranking of the alloys by the parameters is shown as well. The parameter T_{rg} has excellent agreement with GFA predicted from the Thermo-Calc simulation. Alloys corresponding to a minimum in both liquidus and solidification range all have the best GFA, with GFA decreasing

as the composition deviates from the minima. The region with a minimum in only solidification range has lower GFA, which agrees well with observations made during alloy production, as some crystallinity was confirmed. The alloys that correspond only to a very shallow minimum in liquidus had insufficient GFA to remain amorphous.

Composition	Trg	ΔT_{xg}	γm	Rank by	Rank by	Rank
				\mathbf{T}_{rg}	$\Delta \mathbf{T}_{\mathbf{xg}}$	by γ _m
$(Fe_{70}Ni_{30})_{80}B_{12.5}Si_7Nb_{0.5}$	0.432	0	0.432	1	11	9
$(Fe_{70}Ni_{30})_{80}B_{14}Si_5Nb_1$	0.417	22	0.457	2	3	1
$(Fe_{70}Ni_{30})_{80}B_{15}Si_3Nb_2$	0.415	21	0.453	3	4	2
$(Fe_{70}Ni_{30})_{80}B_{14.5}Si_4Nb_{1.5}$	0.413	20	0.449	4	5	4
$(Fe_{70}Ni_{30})_{80}B_{18}Si_0Nb_2$	0.411	15	0.438	5	7	7
$(Fe_{70}Ni_{30})_{80}B_{17}Si_0Nb_3$	0.408	13	0.431	6	9	10
$(Fe_{70}Ni_{30})_{80}B_{16}Si_0Nb_4$	0.407	16	0.436	7	6	8
$(Fe_{70}Ni_{30})_{80}B_{16.5}Si_{0.5}Nb_3$	0.405	14	0.430	8	8	11
$(Fe_{70}Ni_{30})_{80}B_{16}Si_1Nb_3$	0.404	21	0.442	21	4	6
$(Fe_{70}Ni_{30})_{80}B_{15.5}Si_2Nb_{2.5}$	0.401	26	0.448	10	2	5
$(Fe_{70}Ni_{30})_{80}B_{13}Si_2Nb_5$	0.387	13	0.409	11	9	13
$(Fe_{70}Ni_{30})_{80}B_{15}Si_1Nb_4$	0.387	7	0.399	11	10	16
$(Fe_{70}Ni_{30})_{80}B_{14}Si_1Nb_5$	0.383	41	0.452	12	1	3
$(Fe_{70}Ni_{30})_{80}B_{15}Si_0Nb_5$	0.383	15	0.408	12	3	14
$(Fe_{70}Ni_{30})_{80}B_{14}Si_0Nb_6$	0.379	13	0.401	13	9	15
$(Fe_{70}Ni_{30})_{80}B_{12}Si_3Nb_5$	0.378	20	0.412	14	5	12
$(Fe_{70}Ni_{30})_{80}B_5Si_7Nb_8$	0.371	0	0.371	15	11	17
$(Fe_{70}Ni_{30})_{80}B_4Si_{8.5}Nb_{7.5}$	0.351	0	0.351	16	11	18

Table 3.2. GFA parameters obtained from DSC data, as well as ranking of the alloys by predicted GFA.

 ΔT_{xg} , and γ_m show trends that do not agree well with those of T_{rg} or simulation results. This can be explained by the fact that both T_g and T_x change little between the alloys, exaggerating error in measurement of T_g . The signature of the glass transition is not fully separate from that of crystallization in these alloys, making very precise measurement difficult, with an error approximately +-10 °C, compared to an estimated less than +_3 °C for measurement of T_c and T_x . In T_{rg} , the much larger change in liquidus temperature between the alloys dominates, so this parameter more accurately represents GFA in these alloys. A large temperature difference between glass transition and crystallization temperature (ΔT_{xg}) simplifies thermomechanical forming and stamping operations. Some of the alloys had fairly large ΔT_{xg} , as high as 41 °C for (Fe₇₀Ni₃₀)₈₀B₁₄Si₁Nb₅. A map of ΔT_{xg} is shown in Fig. 3.9.



Figure 3.9. ΔT_{xg} , vs. composition.

The effects of glass forming elements on T_c was measured by DSC as well, since the Curie temperature of the alloy determines it maximum operating temperature Results are shown in Fig. 3.10. A slight increase followed by a decrease in the slope of the heating curve was seen in all alloys in the DSC results. Si was found to have little effect on T_c , while B and Nb were found to have significant but opposite effects, with B generally increasing, and Nb decreasing T_c . O'Handley [120,121] discusses the effects of B on T_c in Fe-based amorphous alloys, while the effects of Nb are discussed in Aronhime et al [25]. T_c increases, then levels off when increasing the parameter B/Nb, where B is atomic percent B and Nb is atomic percent Nb, as seen in Fig. 18.



Figure 3.10. Change in T_c with B/Nb ratio.

3.10. *Conclusions*

The method of using Thermo-Calc to locate minima in liquidus temperature and solidification range has been successfully demonstrated, and experimentally shown to be able to identify compositions with good GFA. Depth of liquidus minimum and solidification range magnitude have been shown to correlate well with the most widely used GFA parameter, T_{rg} , obtained from calorimetry. Difficulty in measuring T_g with high precision resulted in parameters that are strongly influenced by T_g , such as ΔT_{xg} and γ_m to be less conclusive.

In future alloy development, this method will allow screening of an entire ternary composition range, and rapid identification of alloys with the highest GFA. This will accelerate alloy development and allow optimization of existing amorphous and MANC systems.

4. Optimized Alloys with Higher Magnetic Element Content

The results of Ch. 3 confirmed the utility of Thermo-Calc simulation in MANC development. Having developed a way to predict glass forming ability across a composition space, it will be possible to reduce the content of the glass forming elements, increasing the magnetic element concentration, and improving B_s and T_c . Identifying the compositions with the best GFA will compensate for the reduction in GFA from the lower glass former content. Recent work has explored alloys with increased magnetic element content in an attempt to improve magnetic properties. Additionally, reduction of transition metal glass formers can result in even higher increases in B_s , since these elements introduce an anti-ferromagnetic exchange and reduce saturation beyond simple dilution [122]. Unfortunately, low transition metal content can result in excessive grain growth. McHenry and Laughlin [5] explain the grain growth retarding effect of TMs by showing how these elements are rejected to the residual amorphous phase, with and overlap and resulting impingement of these enriched regions.

Recently, Parsons et al [122] and Suzuki et al [123] proposed a different mechanism for Febased alloys without TMs. In these, nucleation begins below T_g . This results in a very slow, but still non-zero diffusion rate, and furthermore crystallization favors heterogeneous nucleation, which also explains why Cu additions are effective in Fe-based alloys. TM additions stabilizes the amorphous phase, shifting T_x above T_g , where crystallization kinetics are enhanced by viscous flow, and a rapid increase in homogeneous nucleation density results. To prevent excessive grain growth in alloys with low TM content, some recent work has explored the use of very high heating rates during annealing, which has been shown to allow to result in fine grain size without TM additions. [123,124]

4.1. Thermo-Calc Modeling and DSC Results

Since the goal of amorphous soft magnetic alloy development is to reduce the content of glass formers in order to improve the magnetic properties, additional simulations of the $(Fe_{70}Ni_{30})_{100}$, $x(B-Si-Nb)_x$ system were performed at x=18 and x=15. The results are shown in Fig. 4.1, along with all compositions produced within this range. Both show deep minima in liquidus temperature at high B concentrations, but with little to no corresponding minimum in solidification range. These alloys are therefore expected to have significantly lower GFA.



Figure 4.1. (a) Liquidus T of $(Fe_{70}Ni_{30})_{100-x}(B-Si-Nb)_x$ (x=18). (b) Solidification range $(Fe_{70}Ni_{30})_{100-x}(B-Si-Nb)_x$ (x=18). (c) Liquidus T of $(Fe_{70}Ni_{30})_{100-x}(B-Si-Nb)_x$ (x=15). (d) Solidification range of the $(Fe_{70}Ni_{30})_{100-x}(B-Si-Nb)_x$ (x=15). Dots show alloys made.

Based on the above simulation results, alloys of the compositions $(Fe_{70}Ni_{30})_{82}B_{15}Si_0Nb_3$, $(Fe_{70}Ni_{30})_{82}B_{16}Si_0Nb_0$, $(Fe_{70}Ni_{30})_{82}B_{16}Si_1Nb_1$, $(Fe_{70}Ni_{30})_{85}B_{14.5}Si_0Nb_{0.5}$ were produced. The compositions were chosen based on minima in the liquidus, though these alloys did not show

minima in solidification range. T_c , T_g , T_{x1} , and T_{x2} were determined by DSC. Saturation magnetization was determined by PPMS at 10 K, and Curie temperatures were confirmed by the same method. The results are shown in Fig. 4.2.



Figure 4.2. (a) T_c , T_g , T_{x1} , and T_{x2} as determined by DSC, and (b) saturation induction determined by PPMS.

As seen in the above results, $T_c s$ of the $(Fe_{70}Ni_{30})_{82}$ alloys are high relative to the $(Fe_{70}Ni_{30})_{80}$ alloys tested above. The trend of T_c decreasing with decreasing B and concomitant increasing Nb is seen as well. The saturation magnetization also increased with increasing magnetic element content, reaching a high of 1.48 T for $(Fe_{70}Ni_{30})_{85}B_{14.5}Nb_{0.5}Si_0$, as seen in Fig. 4.3, which represents a significant improvement over previously reported Fe-Ni based alloys, at ~1.2 T [24].



Figure 4.3. (a) B-H loop of (Fe₇₀Ni₃₀)₈₅B_{14.5}Si₀Nb_{0.5} from PPMS measurement. (b) M vs T curve of the same alloy. (c) XRD results of (Fe₇₀Ni₃₀)₈₅B_{14.5}Si₀Nb_{0.5} annealed at various temperatures.

When measuring M vs. T of $(Fe_{70}Ni_{30})_{85}B_{14.5}Nb_{0.5}Si_0$, magnetization declined, indicating approach to the Curie temperature of the amorphous phase, followed by a jump at 425 °C (Fig. 4.3b). The jump occurred within one increment of the measurement (10 °C), indicating a very rapid crystallization process. One possible explanation for the rapid crystallization would be polymorphic crystallization, where the composition of the amorphous material is very close to that of the final crystallization products, and crystallization occurs without long-range diffusion. However, XRD analysis of the alloy annealed at a range of temperatures, shown in Fig. 4.3c, indicate that the alloy crystallizes by a conventional 2-step process, with BCC and FCC phases appearing first, as low as 415 °C, followed by a mixture of Fe₃B and Fe₂₃B₆ ordered phases. This is additionally supported by DSC data, which shows 2 distinct exothermic peaks associated with crystallization. The material was therefore determined to undergo a 2-step crystallization process:

$Amorphous \rightarrow BCC+FCC+Amorphous \rightarrow BCC+FCC+Fe_{3}B+Fe_{23}B_{6}$

The Fe₂₃B₆ phase is a type of 23:6 ordered phase that is commonly seen in secondary crystallization of MANC materials containing Fe, Ni, and Co. The 23:6 phase has been reported to form in the $Cr_{23}C_6$ or $Mn_{23}Th_6$ prototype structures. These structures have the same symmetries, but different sites are occupied by large vs. small atoms. The $Cr_{23}C_6$ phase forms in B-rich alloys, and consists of smaller B atoms occupying octahedral sites, while the $Mn_{23}Th_6$ structure occurs in alloys with greater concentrations of large transition metals such as Zr and Nb. Here, the large atoms occupy the octahedral sites. The 23:6 phase is often metastable when it occurs. [125,126]

4.2. Effects of Annealing on Magnetic Properties

Samples were annealed at temperatures starting at slightly below their T_{x1} temperatures, and the effects on coercivity and B_s were plotted in Fig. 4.4. The crystallization onset line here is marked where the loops became noticeably squarer and does not perfectly correspond to T_{x1} temperatures from DSC. The reason for the disagreement with crystallization results from DSC is the different heating rates during annealing. The annealed samples were heated at 10 °C/min, vs. 40 °C/min in the DSC, resulting in lower crystallization onset. All as-cast samples started at coercivities of 30-40 A/m. (Fe₇₀Ni₃₀)₈₂Nb₁Si₁B₁₆ shows coercivity increasing continuously with annealing, which is

typical for alloys with low Nb content, due to grain coarsening. $(Fe_{70}Ni_{30})_{82}Nb_2Si_0B_{16}$ and $(Fe_{70}Ni_{30})_{82}Nb_3Si_0B_{15}$ show a large drop in coercivity, down to 16-17 A/m, with annealing, and the points corresponding to lowest coercivity and/or highest B_s are marked as optimal anneal. The $(Fe_{70}Ni_{30})_{85}Nb_{0.5}Si_0B_{14.5}$ alloy exhibits increasing coercivity followed by a small drop shortly before crystallization onset, but coercivity of all annealed samples was very high.



Figure 4.4. Coercivity of (a) $(Fe_{70}Ni_{30})_{82}B_{16}Si_1Nb_1$, (b) $(Fe_{70}Ni_{30})_{82}B_{16}Si_0Nb_2$, (c) $(Fe_{70}Ni_{30})_{82}B_{15}Si_0Nb_3$, and (d) $(Fe_{70}Ni_{30})_{85}B_{14.5}Si_0Nb_{0.5}$ alloys vs. annealing temperature.

The effects of annealing on saturation are shown in Fig. 4.5. All samples showed a decrease in saturation with crystallization onset, which is unusual. It was suspected that all samples have large volume fractions of nanocrystallization in the as-cast state.



Figure 4.5. Saturation induction of (a) $(Fe_{70}Ni_{30})_{82}B_{16}Si_1Nb_1$, (b) $(Fe_{70}Ni_{30})_{82}B_{16}Si_0Nb_2$, (c) $(Fe_{70}Ni_{30})_{82}B_{15}Si_0Nb_3$, and (d) $(Fe_{70}Ni_{30})_{85}B_{14.5}Si_0Nb_{0.5}$ alloys vs. annealing temperature.

4.3.TEM

TEM was performed on both annealed and as-cast samples. Samples were punched into 3 mm disks. They were then ion milled from both sides using a Gatan PIPS ion milling system. The samples were observed optically until a hole appeared. Images were taken from the electron

transparent regions immediately adjacent to the hole. The suspected presence of nanocrystallization in the as-cast state made the structure of these samples interesting. TEM results of the as-cast samples are shown in Fig. 4.6. The contrast seen in the images is mainly due to scattering. Since these are brightfield images, the placement of the aperture blocks electrons that have been scattered to larger angles, resulting in the contrast seen. (Fe₇₀Ni₃₀)₈₂Nb₁Si₁B₁₆ was nearly fully amorphous, with only slight clustering present, while both $(Fe_{70}Ni_{30})s_2Nb_2Si_0B_{16}$ and (Fe₇₀Ni₃₀)₈₂Nb₃Si₀B₁₅ showed small, uniformly distributed grains in a residual amorphous matrix. It was noted however, that these two alloys appear to have much larger grains present. These were only seen in the thickest part of the TEM specimen and were very difficult to image, due to the sample thickness being near the limit of electron transparency. It appears that some large grains are present, but not uniformly distributed, and are only seen when imaging a large thickness of material. An example of such grains is shown in Fig. 4.7. The most interesting result was (Fe₇₀Ni₃₀)₈₅Nb_{0.5}Si₀B_{14.5}, with very small sub-10 nm grains and a highly uniform residual amorphous matrix. This structure is what is typically only achieved after annealing under optimal conditions. A study by Suzuki et al [127] using and alloy of an (Fe_{100-x}Ni_x)₈₆B₁₄ showed the smallest grain size, significantly below 10 nm, at a composition of x=30, similar to this alloy.



Figure 4.6. TEM results for as-cast (a) $(Fe_{70}Ni_{30})_{82}Nb_1Si_1B_{16}$, (b) $(Fe_{70}Ni_{30})_{82}Nb_2Si_0B_{16}$, (c) $(Fe_{70}Ni_{30})_{82}Nb_3Si_0B_{15}$, and (d) $(Fe_{70}Ni_{30})_{85}Nb_{0.5}Si_0B_{14.5}$ alloys.



Figure 4.7. Example of coarse grains seen in thicker regions of as-cast $(Fe_{70}Ni_{30})_{82}Nb_2Si_0B_{16}$ and $(Fe_{70}Ni_{30})_{82}Nb_3Si_0B_{15}$ alloy samples.

TEM images of the annealed samples are shown in Fig. 4.8. $(Fe_{70}Ni_{30})_{82}Nb_1Si_1B_{16}$ had distributed grain sizes up to 50 nm. The low Nb content allowed excessive coarsening during annealing. $(Fe_{70}Ni_{30})_{82}Nb_2Si_0B_{16}$ and $(Fe_{70}Ni_{30})_{82}Nb_3Si_0B_{15}$ both showed grains in the ideal sub-20 nm size, with the latter showing much better uniformity and an excellent annealed structure. This explains the low coercivity achieved by these alloys. Interestingly, the large grains seen in some regions of these 2 samples are no longer seen after annealing. $(Fe_{70}Ni_{30})_{85}Nb_{0.5}Si_0B_{14.5}$ showed very large grain coarsening.



Figure 4.8. TEM results for annealed (a) $(Fe_{70}Ni_{30})_{82}Nb_1Si_1B_{16}$, (b) $(Fe_{70}Ni_{30})_{82}Nb_2Si_0B_{16}$, (c) $(Fe_{70}Ni_{30})_{82}Nb_3Si_0B_{15}$, and (d) $(Fe_{70}Ni_{30})_{85}Nb_{0.5}Si_0B_{14.5}$ alloys.

Crystallization in MANC materials follows 1 of 3 mechanisms. In primary crystallization, typically seen in commercially useful materials, the crystalline phase that forms is rich in magnetic elements, while glass formers are rejected into the residual amorphous matrix. This stabilizes the

amorphous structure, resulting in smaller nanocrystals surrounded by a residual amorphous matrix. At higher temperatures, this is followed by secondary crystallization, and the amorphous matrix is converted to ordered intermetallics. A second mechanism is eutectic crystallization, where the composition of the amorphous material is exactly a eutectic composition. Here, crystallization proceeds in a single step, with complete crystallization to a lamellar 2-phase crystalline state. A third mechanism is polymorphic crystallization, where the composition of the amorphous material is close to that of a stable intermetallic compound. Crystallization proceeds very rapidly to a single phase, with minimal long-range diffusion. [5]

As the 4 alloys discussed above all had a residual amorphous phase remaining after annealing, as evidenced by the amorphous halo, the crystallization mechanism is primary, followed by secondary crystallization. Since secondary crystallization is highly detrimental to soft magnetic properties, a thorough understanding of its kinetics is necessary to prepare optimal annealing processes and determine material lifespan in various operating temperatures. Such kinetics studies have been performed for the MANC materials, and will be a subject of future work. [128]

4.4.Commercially cast alloy

Commercial application of a new MANC material will require casting on a large scale, both in width and length of the ribbon. Large ribbon width will allow stamping, winding, or forming larger components necessary for high power applications, while longer casting lengths will increase productivity. The laboratory caster is limited to 5 mm ribbon widths and lengths <100 m. to test the adaptability of this alloy to large scale production, and to provide better ribbon quality, both to measure improvements in magnetic properties and to create a more consistent sample for future microscopy work, a length of 2" wide ribbon was cast by Metglas on a commercial caster. The

ribbon was measured on a profilometer to determine thickness, with results shown in Fig. 4.9. The ribbon averaged 25.4 μ m thick, which was thicker than the 19 μ m ribbon cast at CMU.



Figure 4.9. Profilometry data for the Metglas cast of the 85% alloy.

XRD was performed on the air and wheel side of the ribbon (Fig 4.10). The wheel side showed evidence of very fine nanocrystallization, as evidenced by the very broad first peak incorporated into the distributed amorphous peak. A small FCC 200 peak, typically associated with textured surface crystallization, was seen as well. The air side showed evidence of more extensive crystallization, with further FCC peaks emerging. The large thickness of the ribbon resulted in lower cooling rate, leading to pronounced crystallization away from the wheel.



Figure 4.10. XRD results of the wheel (top) and air (bottom) side of the ribbon.

4.5. Magnetic properties of commercially cast alloy

Magnetic properties were measured by strip testing of the as-cast strip. B-H loops, shown in Fig. 4.11a indicate a saturation induction of up to 1.42 T, very close to that seen in the CMU alloy (1.48 T). Coercivity vs. induction, shown in Fig 4.11b show coercivity in the 30-45 A/m range in the middle of the B-H loop, similar but slightly higher than the CMU alloy. Permeability was ~1200 (Fig. 4.11c).



Figure 4.11. Summary of strip testing results. (a) BH loops of as-cast Metglas alloy. (b) Coercivity vs. induction. (c) Permeability at 2 magnetizations.

Since most applications of MANC ribbons involve winding into a core, the magnetic properties of the wound core were measured, and are shown in Fig. 4.12. Coercivity was shown to double, and the core saturated at much higher applied field. Induced stresses when winding are believed to be the cause of increased coercivity, due to magnetostrictive effects. Such magnetostriction induced losses have been noted for other MANC alloys. Byerly et al [1] has explored the reduction of such losses by reannealing the toroidal cores after winding. They found that reannealing above the amorphous Curie temperature but below T_{x1} results in significant increase in magnetic softness, increasing permeability and reducing coercivity. Coercivity was found to depend on anisotropy field H_k , with anisotropy field increasing due to coupling of induced stress in the amorphous phase and magnetostriction in the nanocrystals. Above T_c (amorphous), magnetic anisotropy in the

amorphous state disappears, resulting in a sharp drop in coercivity. [1] Similar results have been reported by Kernion et al [129] in cold rolled MANC material, where annealing between $T_{c(amorphous)}$ and T_{x1} resulted in the lowest coercivity.



Figure 4.12. (a) Change in B-H loop when winding into a core. (b) Anisotropy field strength and permeability in an Fe-Ni alloy vs. re annealing temperature, showing the effect of annealing above $T_{c(amorphous)}$. [1] (c) Coercivity vs. re annealing temperature in the same alloy. [1]

4.6. *Conclusions*

Magnetic properties of the (Fe₇₀Ni₃₀)₈₂Nb₂Si₀B₁₆ and (Fe₇₀Ni₃₀)₈₂Nb₃Si₀B₁₅ are excellent, showing low coercivity and improved saturation vs. previous Fe-Ni alloys. (Fe₇₀Ni₃₀)₈₅Nb_{0.5}Si₀B_{14.5} showed excellent improvement in B_s of 1.48 T, but coercivity could stand to be somewhat improved. In contrast, FINEMET, a long-time industry standard, has a B_s of 1.23 T and coercivity of 2.5 A/m [130], while the coercivity is significantly better, the extremely poor mechanical properties make FINEMET not useful for rotating motor components [31]. Additionally, the saturation induction is lower.

The previously demonstrated Thermo-Calc modeling method was successfully used to identify alloys with sufficient GFA and improved B_s . However, GFA was not expected to be very high in these alloys, as the minima in liquidus and solidification range were small.

With reductions in glass forming elements, GFA was marginal, especially in the 85% alloys. This was seen in the presence of crystallization in the as-cast state. Better process controls and thinner ribbons, both of which are possible on commercial scale casters, should allow this crystallization to be eliminated. Alternatively, it may be possible to produce the alloy in the partially crystallized state. This would greatly simplify manufacturing, since it would eliminate the need for a complex rapid annealing step otherwise necessitated by the low TM content of this alloy. The excellent structure and good magnetic properties of the 85% alloy are encouraging for this possibility. The coercivity of this alloy in the as-cast state was good but may need to be further improved to make this alloy promising as a commercial alloy.

The presence of coarse surface crystallization is believed to play a role in raising the coercivity. The need to characterize this surface crystallization, as well as the need to explain the

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disappearance of the coarse grains in the 82% alloys when annealed, suggest that a cross-sectional TEM profile of the as-cast samples should be performed to develop a better idea of grain size distribution of surface vs. bulk. This will be the subject of future work.

While ribbon quality was significantly improved over the CMU cast, the increased thickness resulted in significant surface crystallization, which resulted in very similar, and slightly higher coercivity. Saturation induction was very similar, at 1.42 T. The moderate permeability of ~1200 is useful for many applications, but a higher permeability is desirable for motor applications. A second cast will be performed, aimed at reducing thickness into the 16 μ m range, which should reduce surface crystallization. This is believed to result in improved coercivity and permeability, while retaining a high B_s. Metglas has recently completed a cast of this alloy with between 14 and 17 μ m thickness. The 17 μ m showed curvature in the ribbon, believed to be due to shrinkage caused by surface crystallization, while this was absent in the 15 and 14 μ m sections, indicating microstructural differences. Structural characterization of these samples will be the subject of future work.

The reduction in magnetic properties in wound cores is believed to be due to magnetostrictive effects. We are exploring the possibility of annealing core after winding to relieve induced stress. However, annealing results have shown that annealing even at temperatures significantly below T_x result in coercivity increases. A very low temperature anneal with long annealing times will be explored.

5. Benchmarking Commercial 2605CO Alloy

The 4 alloys developed in Ch. 4 show high B_s and T_c , and moderate coercivity in their optimally annealed state (as cast in the x=15 alloy). The as-cast x=15 alloy was especially promising for motors applications due to very high B_s . Additionally, mechanical properties were observed to be superior to other MANC alloys (unpublished results). It is useful to compare performance of the above Fe-Ni alloy to a state-of-the-art commercial alloy.

Metglas 2605CO was chosen for benchmarking due to its excellent mechanical properties and very high saturation induction. Current work by the group involves a high speed, MANC-based flux switching motor with a 1.4 kHz switching frequency. The material requirements involve minimum losses at this frequency, and a high saturation induction. B_s of existing alloys has been found to be insufficient, as some regions of the soft magnetic material in the current motor design exceed 1.4 T, saturating the Fe-Ni alloy used. [21]

Metglas 2605CO is a Fe-Co-Si-B alloy developed by Metglas to have higher saturation induction than existing Fe-based alloys. Its composition in mole % is $Fe_{67}Co_{18}B_{14}Si_1$. Lacking a TM growth inhibiting element such as Nb, the alloy is typically used in its amorphous form, with only a low temperature anneal for stress relieving purposes. However, to achieve maximum B_s potential, we annealed the alloy to achieve crystallization. Saturation induction of the as-cast alloy is reported to be 1.66 T. [131]

5.1. Transformation temperatures

The transformation temperatures, such as T_c , T_{x1} , and T_{x2} were determined by DSC. The results are shown in Fig. 5.1. T_{x1} was 425 °C and T_{x2} was 530 °C. Curie temperature was not seen on the DSC curve, indicating T_c of the amorphous phase is higher than crystallization temperature.



Figure 5.1. DSC curve of 2605CO.

To determine the T_cs of the amorphous and crystalline phases, as well as to study higher temperature transformations, a M vs. T curve was generated by vibrating sample magnetometry (VSM) at a constant field of 1 kG and between 150 and 850 °C. The results are shown in Fig. 5.2. Both T_x temperatures are very close to those measured by DSC. At ~630 °C, a hump is seen in the curve, labeled 3 in Fig 5.2. This corresponds to the $\alpha' \rightarrow \alpha$ Fe transition at this composition (Fig. 5.2). [15] The magnetization does not reach zero and begins to rise again at above ~720 °C, labeled 4 in Fig. 5.2. This is suspected to be due to initially Fe-rich nanocrystalline phases forming, which enrich in Co at high temperature.



Figure 5.2. Heating and cooling M vs. T curve of 2605CO.



Figure 5.3. Fe-Co Phase diagram. [15]

5.2. Stress Relief Annealing

Strips were annealed at primary crystallization completion (420 °C), onset of secondary crystallization (450 °C), and completion of secondary crystallization (500 °C). XRD results are shown in Fig. 5.4. Both the 420 and 450 °C samples had a fully BCC or α ' structure, while the 500 °C sample had additional Fe₃B or Fe₂₃B₆ structures. The 23:6 structure has been previously reported in secondary crystallization of MANCs. [125,126]


Figure 5.4. XRD curves of samples annealed at 420 °C, 450 °C, and 500 °C.

Strip testing results for these samples are shown in Fig. 5.5. Both the 420 and 450 °C had very high saturation inductions of 1.7 T, but coercivities were ~600A/m. Secondary crystallization resulted in a reduction of B_s to 1.5 T, and very high coercivity of 2000 A/m.



Figure 5.5. Strip testing results of the 2605CO alloy annealed, at completion of primary crystallization (420 °C), onset of secondary crystallization (450 °C), and completion of secondary crystallization (500 °C).

5.3. Conclusion

Thermal and phase transformation behavior of 2605CO were studied and optimal annealing parameters were determined. The saturation induction of 2605CO after primary crystallization is very high, at 1.7 T, but coercivity is excessive for medium frequency applications, including high speed motors. Coercivity in the primary crystallized state limits applications to frequencies below 1 kHz. This alloy also has a fairly high magnetostriction coefficient of 33 ppm. This will lead to higher losses in a high frequency AC application, especially if stress is induced during winding. Losses due to induced stress can be partially mitigated by annealing after winding and will be discussed further in Ch. 8.

6. Formability

Efforts to construct electric motors out of amorphous and MANC materials have either used radial or axial topologies. In radial motors, a magnetic flux path extends radially from the rotor. The rotor and stator are made by stacking layers of a magnetic material, which must be cut into shape. The thickness of amorphous and MANC ribbon poses a manufacturing challenge, since potentially 1000s of layers must be cut and stacked, and the material's hardness results in excessive tool wear [132]. Such motors [16,22,133] have been built using amorphous and MANC materials. Silveyra et al [16] used laser cutting to produce the individual lamination layers, but large scale manufacturing will require enhanced formability for stamping. A radial motor and section of stator lamination is shown in in Fig. 6.1a and 6.1b.



Figure 6.1. (a) A radial design permanent magnet motor. (b) A single layer of stator magnetic material, showing the complex geometry [16]. (c) A wound and machined stator core made from amorphous ribbon [17].

An axial motor design has a flux path parallel to the rotational axis. These motors were found to be readily adaptable to amorphous and MANC materials, since the rotor and stator can be produced by winding the ribbon into toroids [17,21,134–136]. Formability is less critical for axial motors, since the wound stator and rotor can be cut or machined to shape after winding, (Fig. 6.1c) but increased formability may allow decreased machine tool wear and stamping before winding.

Complex rotors and stator geometries in of both designs may make it advantageous to process the material by hot forming and stamping. Schroers et al [137,138] have demonstrated hot forming of amorphous material by blow molding. Other researchers have demonstrated forming by pressing into dies at high temperatures [139–144]. The most important factor for formability is the temperature range between glass transition and crystallization. Much below the glass transition temperature, the material does not undergo homogeneous deformation, while above it, it can exhibit viscous flow with very large plastic strain [145,146]. The viscosity above T_g is given by the Vogel-Fulcher Tamman equation:

$$\eta = \eta_0 \exp\left(\frac{DT_0}{T - T_0}\right)$$
[Eq. 6.1] [81,82,147]

Where D is a fitting parameter and T_0 is a parameter typically within about 50 K of T_g . As seen in this equation, dramatic reduction in viscosity is possible with even a small increase in temperature above T_g . Above the crystallization temperature, crystallization will impede further deformation. The temperature range between glass transition and crystallization is ΔT_{xg} and is known to increase with increasing GFA [87]. The alloys developed in Ch. 4 has fairly low ΔT_{xg} of 12-23 °C, so successful efforts to improve formability range will benefit these alloys.

Z. Lu and J. Li [85] Showed that T_g is proportional to the average melting point of the alloying elements. They proposed a linear relationship:

$$Tg = 0.385 < Tm >$$
 [Eq. 6.2] [85]

However, the correlation is not strong. A more accurate approximation was made by Cao et al [148]. They found that T_g is proportional to the eutectic melting temperature of a binary alloy of the main constituent elements by:

$$Tg = 0.55T_{m(AxBy)}$$
 [Eq. 6.3] [148]

They explained this by T_g being dominated by interactions between solute atoms at the centers of atomic clusters and their surrounding solvent atoms. Wang [149] found that a linear correlation between T_g and Young's modulus exists.

There are fewer studies into the effect of alloying on T_x than T_g . Elements that increase GFA generally also increase T_x , as shown by Naohara [150]. They showed that the increase in T_x depended on the atomic size of the alloying elements. Alloying additions with larger atoms tended to result in greater increases in T_x . Gheiratmand et al [51] studied the effects of several transition metal additions on T_x , with both increases and decreases seen, but no explanation has been proposed. Donald and Davies [47] studied the effects of transition metal additions on crystallization temperatures in Fe-based amorphous alloys. The found that T_x increase partially depends on cohesive energy of the added transition metal, and that it correlates well with electrons per atom in the alloy. A smaller number of d electrons was believed to result in stronger, more thermally stable bonds. It should be noted that the effectiveness of the additions also depended very strongly on atomic radius, and this size difference will contribute to increased GFA, contributing to stability against crystallization.

6.1. The effects of transition metal additions on formability

Previous work has explored the addition of transition metals to MANCs for the purpose of increasing resistivity by the formation of virtual bound states [25,151]. Examination of the first 2 rules of glass formability [91] reveals that the addition of an additional element should increase GFA as well. The addition of these elements can therefore have multiple benefits, lowering losses, improving GFA, and increasing the formability range. Unfortunately, all these additions result in decreased B_s and T_c , so magnetic properties need to be balanced against the benefits.

Additions of Cr, Ga, Mn, Mo, Ti, and V were added at concentrations of 0.5, 1, 3, and 5%. And the ΔT_{xg} was measured by DSC. Effects on magnetic properties were observed by measuring change in T_c. Results are shown in Fig. 6.2. All additions, except for 0.5% Ga, resulted in a decrease of T_c. In the case of Mo, Ti, and V, additions of over 3% resulted in T_c falling below room temperature. The most significant increases in ΔT_{xg} occurred with 0.5% additions of Mo (ΔT_{xg} =75 K) and Ti (ΔT_{xg} =94 K), with only slight decrease in T_c.





Figure 6.2. The effects of TM additions on $T_{c},\,T_{g},\,\text{and}\,\,T_{x}.$

6.2. Conclusions

Useful increases in ΔT_{xg} and resulting formability can be achieved with small additions of Mo and Ti. Other elements can also result in large increases, but in concentrations that will severely degrade magnetic properties.

7. JMAK Kinetic of Fe-Ni Crystallization

MANC alloys typically attain optimal magnetic properties by annealing to induce nanocrystallization. Annealing on a laboratory scale is typically done in a furnace, with adequate time given to ensure that temperatures equalize throughout. On a commercial scale, large lengths of ribbon will need to be annealed in a short time. A pilot commercial-scale annealer was built at CMU, which relies on ribbon being continuously fed through a furnace, which heats the ribbon by thermal conduction rather than convection or radiation. This results in large differences between the heating rates and dwell times seen on a lab vs. commercial scale. The ability to consistently anneal the material to the same degree of crystallization will require a thorough understanding of crystallization kinetics. In the case of the x=15 alloy discussed in Ch. 4, which has been cast in an already crystallized state, annealing to induce crystallization may not be required. However, a stress-relief anneal after winding will be necessary to reduce magnetostriction induced losses. This will also require understanding of crystallization kinetics to prevent further grain growth.



Figure 7.1. Commercial scale annealing line at CMU.

7.1. Johnson-Mehl-Avrami-Kolmogorov Kinetics

Johnson-Mehl-Avrami-Kolmogorov (JMAK) kinetics were developed independently by Johnson, Mehl, and Avrami in the United States and Kolmogrov in the Soviet Union. JMAK kinetics describe the rate of transformation where the reaction is a function of time and temperature. The variable X describes the fraction of a new phase that has formed. The rate then depends on the amount of remaining parent phase (1-X). Assuming that the reaction is thermally activated:

$$\frac{dX}{dt} = k(t)(1 - X)$$
[Eq. 7.1] [152]

Where k(t) is a function that describes the temperature dependence of transformation. Integrating from t=0 to a time t:

$$X = 1 - \exp(-kt)$$
[Eq. 7.2] [152]

Where k is a temperature dependent rate constant:

$$k = k_0 \exp\left(\frac{-Q}{k_b T}\right)$$
 [Eq. 7.3] [152]

Where k_0 is the attempt frequency, Q is activation energy, and k_0 is Boltzmann's constant. This gives the temperature dependence of the growth rate.

In the simpler case, usually describing a phase transformation in a single component system, the growth rate depends only on diffusional jumps between phases and depends linearly on temperature. Here, the JMAK equation can be written as:

$$X = 1 - \exp(-kt^n)$$
 [Eq. 7.4] [152]

With n taking integer values of 1-4. To see why this is the case we can look at a spherical particle growing, with α as the parent phase and β as the product. Growth rate (G) will equal the interfacial velocity (v):

$$G = v = \frac{dr}{dt}$$
 [Eq. 7.5] [152]

Assuming immediate nucleation, the volume of a single particle is:

$$V = \frac{4}{3}\pi r^3 = \frac{4}{3}(vt)^3 = \frac{4}{3}(Gt)^3$$
 [Eq. 7.6] [152]

If nucleation does not occur immediately, the above becomes:

$$V = \frac{4}{3}(v(t-\tau))^3 = \frac{4}{3}(G(t-\tau))^3$$
[Eq. 7.7] [152]

Where τ is the time delay. The total number of nuclei is then Nd τ . Overall transformation is then:

$$X = \frac{4}{3}\pi NG^3 \int_0^t (t-\tau)^3 d\tau = \frac{\pi}{3}NG^3 t^4$$
 [Eq. 7.8] [152]

Thus, n attains a maximum value of 4 from nucleation + 3-dimensional growth. 2-dimensional and 1-dimensional growth will reduce n by 1 and 2, respectively, while nuclei being already present reduces n by 1.

In multicomponent alloys, the transformation rate is often limited by a diffusion barrier between the 2 phases. Rate here will be additionally constrained by diffusion through the barrier. Starting with Fick's second law:

$$\frac{\partial J}{\partial t} = -D \frac{\Delta C}{x} = \frac{\partial x}{\partial t}$$
[Eq. 7.9] [152]

Where x is diffusion distance, D is the diffusion coefficient, and ΔC is the concentration difference.

$$\int_{0}^{x} x dx = -D\Delta C \int_{0}^{t} dt$$
[Eq. 7.10] [152]

$$x^{2} = -D\Delta C t = \text{kt}$$
[Eq. 7.11] [152]

$$x = k t^{0.5}$$
[Eq. 7.12] [152]

The presence of a diffusional barrier thus contributes an extra n=0.5 value. n then take on values between 0.5 and 2. In the Case of MANCs, where we can assume that nuclei are present from the beginning, and growth is 3-dimensional, n is generally $\sim 3/2$. [153] A summary of Avrami exponents and types of transformations that they represent is shown in Table 7.1.

	No New Nucleation	Continuous Nucleation	No New Nucleation + Diffusion Barrier	Continuous Nucleation + Diffusion Barrier
1D Growth	1	2	1/2	1
2D Growth	2	3	1	3/2
3D Growth	3	4	3/2	2

Table 7.1. Summary of Avrami exponents for different nucleation and growth types.

In MANC materials, as the crystals continue to grow, the growth rate slows due to soft impingement of the diffusion barriers. The growing crystals reject the glass forming elements into the remaining amorphous material. Eventually, these enriched regions overlap, reducing driving force for crystallization. this results in the observed s-shape of the crystallization curve, with a flattening at longer times. An illustration of soft impingement is shown in Fig. 7.2.



Figure 7.2. Illustration of soft impingement. C_0 is the initial glass former concentration, $C_{crystal}$ is the concentration in the growing crystals, and C* is the concentration at the boundary between amorphous and crystalline. Redrawn from [5]

7.2. JMAK Kinetics of (Fe70Ni30)80B14Si2Nb4

JMAK kinetics of (Fe₇₀Ni₃₀)₈₀B₁₄Si₂Nb₄ has previously been explored by Aronhime et al [154] using DSC, with a TTT diagram developed for primary crystallization. However, a method of using isothermal VSM measurements at constant field has been found to be more accurate, so these results are revisited in this chapter. The choice to start with (Fe₇₀Ni₃₀)₈₀B₁₄Si₂Nb₄, rather than the newer alloys developed in Ch. 4 is due to the absence of crystallization in the as-cast state, which will simplify analysis. This alloy will be used as a starting point, and JMAK kinetics of the new alloys will be determined in future work.



Figure 7.3. (a) VSM magnetization vs. heating curve of $(Fe_{70}Ni_{30})_{80}B_{14}Si_2Nb_4$, showing Curie temperature of the amorphous phase, and a separate jump due to crystallization. (b) VSM Cooling curve after a 3 h dwell time at 460 °C.

A magnetization vs. temperature curve was generated using the Lakeshore VSM with the furnace installed. A field of 1 kG was applied, which was enough to saturate the samples. The $(Fe_{70}Ni_{30})_{80}B_{14}Si_2Nb_4$ was cut into 3 mm disk samples of 1.3 mg mass and glued to the end of a quartz rod with high temperature adhesive. The sample was heated to 800 °C to determine Curie temperatures and crystallization temperatures. Fig. 7.3a shows the M vs. T heating curve of this alloy. T_c of the amorphous phase was shown to be 355 °C, which is significantly below primary crystallization temperature. The primary crystalline phase is magnetic and has a high Curie temperature of ~630 °C. Therefore, if the sample is heated above this T_c of the amorphous phase, any magnetization will be entirely due to the presence of primary crystals. No evidence of the secondary crystalline phases is seen even at 800 °C, indicating that they are paramagnetic at these temperatures. A second VSM run was performed on a new sample, which was heated to 460 °C for 3 h. this temperature is low enough to avoid secondary crystallization, and the dwell time is long enough to ensure full primary crystallization. the cooling curve is shown in Fig. 7.3b. This

curve will allow the magnetic moment of a fully crystallized sample to be determined at different temperatures, compensating for Curie effects.

7 samples were then held isothermally at 420, 425, 430, 435, 440, 460, and 480 °C in a 1 kG field, and magnetization recorded. Results are shown in Fig. 7.4a. Only the 480 °C sample completed primary crystallization. Fig. 7.4b shows the results normalized using the cooling curve from Fig. 7.3b. at each temperature, the magnetization on the curve was taken to correspond to fully crystallized.



Figure 7.4. (a) Isothermal magnetization curves showing crystallization. Curves are normalized to the highest magnetization value attained. (b) Same curves normalized to magnetization attained by the fully crystallized sample. The crystallization curves were fitted to the JMAK equation. A slightly modified version of the JMAK equation was used:

$$X = 1 - \exp(-k(t - \tau)^{n})$$
 [Eq. 7.13]

Where τ is a fitting parameter. An example curve fit is shown in Fig. 7.5a, with n and k determined from the fit. Graphs of n and k are shown in Fig. 7.5b and 7.5c. n varied between 0.86 and 0.39,

which is significantly lower than the ~1.5 typically seen in MANC material. The reason for the low n values is not yet explained. k varied between $2x10^{-4}$ and $1.8x10^{-3}$. Due to the very slow crystallization at these temperatures, the curves for 420 and 425 °C were very incomplete, and a curve fit could not be obtained.



As the magnetization vs. temperature experiment allow determination of time necessary for any % crystallized at the temperatures measured, a TTT diagram can be constructed. This is shown in Fig. 7.6.



Figure 7.6. TTT diagram for primary crystallization of (Fe₇₀Ni₃₀)₈₀B₁₄Si₂Nb₄.

7.3. Activation Energy

Activation energy of primary crystallization was estimated using the Kissinger equation. Samples were heated in a DSC at 5, 10, 20, 40, and 60 K/min, and the temperature of peak rate of primary crystallization recorded. Activation energy was determined by the Kissinger equation:

$$\frac{d\ln(\varphi/T_p^2)}{d(1/T_p)} = -\frac{E_a}{R}$$
[Eq. 7.14] [155]

Where φ is heating rate, T_p is peak transformation temperature, and E_a is activation energy. A plot of crystallization temperature vs. heating rate is shown in Fig. 7.7, with E_a determined from the slope to be 3.53 eV. Activation energy for other MANCs were, 3.4 eV [156], 3.8 eV [157], and

4.1 eV [158] for Fe-based alloys, 3.4 eV for Fe-Zr-B-Cu NANOPERM [159], and 2.8 eV – 3.8 eV for Fe-Co-based HITPERM [160–163].

The effects of composition on activation energy, and the mechanisms of these effects are summarized by McHenry et al. [48] Donald and Davies [47] determined that increasing cohesive energy of the amorphous phase by TM additions will increase activation energy for crystallization, due to increased higher thermal stability. Alloying elements that reduce the electrons per atom of the alloy increased the cohesive energy and thus T_x . Additionally, TM additions with large atomic radius further increased activation energy. This was explained by the higher activation energy of a diffusional jump for large atoms, since they must further displace adjacent atoms. Ramanan and Fish [164] observed that in amorphous alloys, Si additions beyond eutectic composition strongly increases E_a . Luborsky and Lieberman [165] determined the effect of B concentration on activation energy in an Fe-B alloy. They found that at ~21% B, B atoms fill all available Bernal holes, analogous to vacancies in a crystalline material. This greatly slows diffusion, leading to a sharp increase in E_a .



Figure 7.7. Peak crystallization temperature vs. heating rate, showing activation energy determined from the slope. [1]

7.4. Conclusions

JMAK kinetics of primary crystallization in (Fe₇₀Ni₃₀)₈₀B₁₄Si₂Nb₄ have been determined by isothermal VSM measurements. The curves showed the expected s-shape, allowing a fit to the JMAK equation to be performed, and the parameters n and k to be determined. The values of k seen fall within the expected range for MANC materials, while n was lower than typical. The reason for the low n values is unknown and will be explored in future work. The activation energy for primary crystallization has been determined by the Kissinger method, and is in the range of other MANC alloys. A similar JMAK study and Kissinger analysis will be performed on the new alloys developed in Ch. 4. This will be the subject of future work.

8. Cross-sectional Transmission Electron Microscopy

Excessively large surface crystallization has been proposed as a possible explanation for the higher than desired coercivity seen in the alloys developed in Ch. 4. To explore this, we proposed cross-sectional TEM to study the structure near the surface and compare with the bulk. Cross-sectional TEM was performed in collaboration with Dr. Charudatta Phatak of Argonne National Lab. Due to time and funding constraints, the initial TEM work was performed on (Fe₇₀Ni₃₀)₈₀B₁₄Si₂Nb₄ samples, though in the future, this work will be extended to the new alloys developed in Ch. 4.

As noted in section 4.5, the coercivity of material that has been wound into a core increases significantly due to stress-induced magnetostrictive loss. The effects of reannealing to reduce magnetostrictive effects were studied by Byerly et al. [1] The results below describe the effect on surface and bulk structure of the reannealing treatment. This reannealing technique and knowledge of its structural effects will be useful for the new, high B_s alloys.

8.1.TEM Results

As noted in section 4.5, the coercivity of material that has been wound into a core increases significantly due to stress-induced magnetostrictive loss. To simulate this, 1 sample was annealed at 440 °C without applied stress, while a second was annealed at the same temperature and 50 MPa. The reannealing temperature was chosen to minimize coercivity. Brightfield and darkfield cross-sectional images were taken at 12000x and 20000x, and a bulk average grain size, surface average grain size, and standard deviations were determined using ImageJ. TEM results are shown in Fig. 8.1. [1]



Figure 8.1. (a) Brightfield, (b) darkfield image and (c) TEM diffraction pattern of the strain-annealed, then reannealed sample at 450°C for 30 minutes and (d) brightfield, (e) darkfield image and (f) TEM diffraction pattern of the conventionally annealed sample at 450°C for 30 minutes. [1]

The surface of both samples shows a thin region, 40 nm thick with much higher crystalline density. A comparison of this grain size and that in the bulk is shown in table 8.1. No significant difference in grain size is noted between surface and bulk, though density of crystallization is much higher in the surface. The samples annealed with and without applied stress showed similar grain sizes, without excessive coarsening due to reannealing. TEM diffraction results revel a mixture of BCC and FCC grains. [1]

	Surface Grain Size	Surface StDev.	Bulk Grain Size	Bulk StDev.
Strain-Anneal + Re-Anneal: 12kx	14.03	10.12	11.48	6.54
Strain-Anneal + Re-Anneal: 20kx	17.88	9.24	15.07	5.74
Conventional Anneal: 12kx	13.92	5.68	11.76	5.59
Conventional Anneal: 20kx	13.97	6.21	14.20	5.26

Table 8.1. A comparison of surface and bulk grain size in the samples annealed with and without applied stress. [1]

8.2. Conclusions

Cross sectional TEM was used to determine structural effects of reannealing in $(Fe_{70}Ni_{30})_{80}B_{14}Si_2Nb_4$, as well as determine the usefulness of the technique for subsequent surface crystallization studies. The method allowed clear determination of the structure of the surface layer. In this alloy, reannealing was not found to result in excessive grain growth when performed at the optimal temperature, and no significant difference was seen between surface and bulk grains. The lack of excessively large surface grains in this alloy will not necessarily translate in similar surface structure in the new alloys developed in Ch. 4. With a lower glass former content in those alloys, surface crystallization may form earlier in the solidification process, giving it more time to grow. The cross-sectional TEM techniques presented here will be used to examine surface crystallization in those alloys in future work.

9. Conclusions and Future Work

In this work, the design and optimization of Fe-Ni based MANC materials by prediction of glass forming ability is presented. 4 new alloys resulted from this work, with sufficient GFA to be successfully cast, and promising magnetic properties. 2 of these alloys could be annealed, resulting in excellent magnetic performance, while 1 was found to have the desired structure in the as-cast state, possibly negating the need for an additional annealing step. These new alloys were compared to an existing state of the art commercial alloy, and found to have significantly lower losses, making these materials better suited for high frequency applications. Additions of transition metals in 0.5 and 1%, specifically Ti and Mo, increased the thermomechanical processing window in Fe-Ni alloys, allowing stamping and forming of ribbon into motor components. JMAK kinetics were determined for a previously developed Fe-Ni alloy, and the method used was demonstrated to be capable of determining kinetic parameters and activation energy. Finally, cross-sectional TEM was shown to be able to identify structure through the sample thickness, especially at the surface.

TEM results revealed features of the structure of newly developed alloys that explains some of the observed magnetic properties. However, the distribution of grain sizes through the ribbon thickness will allow us to determine how much of the coarse grains observed are surface crystallization, which will show which alloys can be improved by thinner ribbon casts. In particular, the 85% alloy showed good magnetic properties, but coercivity could use some improvement. Cross-sectional TEM has been demonstrated on an older Fe-Ni alloy and will be performed on the new alloys to determine grain size distribution through the thickness, and especially the quantity of surface crystallization.

Thinner 85% alloy is currently being cast by Metglas, in an effort to eliminate surface crystallization. Ribbon as thin as 15 μ m has already been cast, with significantly less curvature in

the as-cast ribbon indicating a more uniform structure. Characterization of the structure of these ribbons will be the subject of future work, as well as magnetic and loss measurements.

Due to the excessive coercivity observed when the ribbon is wound into toroidal core, annealing after winding will be attempted. Annealing after winding has been demonstrated to result in improvement in magnetic properties in other alloys with high magnetostrictive coefficients. An optimal annealing schedule, which results in stress relief but avoids grain coarsening will be developed.

Finally, a JMAK study will be performed on the new alloys to construct TTT diagrams. This will allow easy development of annealing schedules since crystallization time at various temperatures will be known. Activation energies will also be determined.

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