Glass Stability and Kinetic Analysis of Iron-Metalloid Bulk Metallic Glass

By

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To my parents, So and Khong-Worasan Santhaweesuk
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Multicomponent Fe-based bulk metallic glasses (BMGs) with a combination of excellent properties such as good soft magnetic properties, high strength, high hardness, and high corrosion resistance have attracted increasing attention both from a basic science research standpoint and due to their industrial application potential. However, many of the elemental additions which lead to the easiest glass formation are expensive. The identification of alloys composed of abundant and inexpensive elements that still retain excellent properties would promote applications for engineering and industry. In short, the development of the Fe-based BMG without any glass-forming metal elements and with high glass forming ability is desired.

This study shows that the thermal stability of the Fe-based alloys can be improved beyond a simple rule of mixtures prediction by utilizing a well-balance multi-metalloid approach. The kinetics aspect of glass-forming ability is studied experimentally for Fe-B-Si-P alloys. The systematic variation in alloy composition gives access to differences in phase selection and the final dimensions of glass formation. Two alloys, representing the best glass-forming composition and the poorest glass-forming composition, were studied in terms of their stability to crystallization, solidification microstructure evolution and
thermal history. The utility of the wedge-casting technique is developed to examine bulk glass-forming alloys by combining multiple temperature profiles of the quenching melt with a measurement-based kinetic analysis of the phase selection competition and critical cooling rate conditions. Based upon direct thermal measurement, microstructural analysis and kinetic modeling, it was found that both representative alloys show a broad spectrum of solidification microstructures which include a critical cooling rate range. The kinetic competition in the formation of certain phases can enhance or detract from the final dimension of bulk glass formation of the representative alloys. Practical strategies in crystallization kinetics analysis and microstructure control are developed to extend the knowledge of phase competition leading to successful synthesis of BMGs. Low cost Fe-metalloid BMGs will provide a great advantage for the transition to commercial applications when material cost is a critical issue.
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1. Introduction

Over the past decade major advances in the synthesis of amorphous alloys have allowed for the identification of an increasing variety of alloys that can be prepared as non-crystalline solids in bulk sizes up to centimeters in thickness [1-3], typically referred to as bulk metallic glasses (BMGs). Since discovering that many Fe-based metallic glasses have excellent soft magnetic properties [4], functional materials in the form of sheet and wire prepared by melt quenching have been utilized in power transmission applications [5]. However, extended application of the Fe-based metallic glasses into other fields is restricted because of size limitations imposed by the high critical cooling rates for glass formation. A schematic diagram in Figure 1.1 presents cooling rate requirement necessary in order to bypass crystallization during cooling for ordinary amorphous alloys (dot curve) and bulk metallic glasses (dash curve). Bulk metallic glasses exhibit lower critical cooling rates and nucleation rates than that of ordinary amorphous. Recently, Fe-based bulk metallic glasses were achieved in a number of systems [6-10] through copper mold casting [9, 11, 12] and fluxing treatments combined with water quenching [13, 14]. In fact, multi-component alloys in the Fe-(Co, Cr, Mo, Ga, Sb)-P-B-C system, glasses were produced with supercooled liquid regions (T\textsubscript{x}-T\textsubscript{g}) spanning 50K.

Studies focused on the initial formation and properties of multicomponent Fe-based BMGs have attracted increasing attention both from a basic science research standpoint and due to their industrial application potential. However, the elemental additions which lead to the easiest glass formation are expensive (e.g. Ga, Nb, Mo, Y, Co
and Ni). High material costs hinder the adoption of these alloys despite the highly sought properties they exhibit. Generally, BMGs have a high thermal stability as indicated by the presence of a wide supercooled liquid region, $\Delta T_x$, defined as the difference in the glass transition and crystallization onset temperatures ($\Delta T_x = T_x - T_g$). Values for $\Delta T_x$ and the saturation magnetization have been listed in Figure 5.2 for some ordinary amorphous and BMGs alloy compositions to reveal that the glass forming metal elements (i.e. Al, Ga, Nb, Mo and Y) and the magnetic elements (i.e. Co and Ni) caused a significant decrease in the saturation magnetization. Therefore, a push to discover alloys composed of abundant and inexpensive elements that still retain excellent properties should have a great advantage for engineering and industry. In short, maximization of the iron content and replacement of more expensive additions with elements like Si is desired.

With these considerations in mind, it has been reported [15-18] that amorphous Fe-B-Si alloys have high Curie and crystallization temperatures as well as a large saturation magnetization in comparison with other Fe-based alloys such as Fe-P-C, Fe-B-C and Fe-P-B. Therefore, amorphous Fe-Si-B alloys are of technological interest. However, these qualities strongly depend on metalloid content and must be balanced by their ease of formation. For example, a maximum ribbon thickness of 250 $\mu$m can be obtained in Fe$_{75}$B$_{15}$Si$_{10}$ [19]. This alloy composition exhibits high crystallization temperature of about 804 K and critical cooling rate of 9.8x10$^5$ K/s [20].

By contrast, the current work demonstrates that a fully amorphous phase has been observed with a maximum cross sectional thickness of about 800 $\mu$m can be formed using Fe$_{76}$B$_{10}$Si$_9$P$_5$ cast with a two dimensional heat flow geometry (wedge-casting).
Furthermore, by adding phosphorus or carbon into Fe-B-Si alloys, a large supercooled liquid region over 50 K before crystallization can be obtained. This discovery shows that the thermal stability of the Fe-based alloys is improved beyond a simple rule of mixtures prediction by utilizing a well-balanced multi-metalloid approach. Since the glass transition temperature, crystallization temperature, melting temperature, liquidus temperature and Curie temperature are sensitive to the alloy compositions, identification of the optimal alloying strategy for glass formation must be tempered by additional glass properties that will allow a transition to broader use.

Apart from the initial formation of the glassy alloys, it is well known that selective precipitation of certain phases can either enhance or detract from the material properties that are sought. The wide variety of microstructures accessible in materials produced by rapid solidification processing dictate that careful study of the crystallization kinetics must also be executed. To these ends, the processing conditions play a major role in determining the selection of specific product phases and morphology archetypes (i.e. eutectic colonies, primary dendrites, etc.). At the same time, the flexibility in microstructure selection represents a key challenge to implementing a coherent guide to the control of processing that will permit an optimization of alloy design and secondary processing routes that may be necessary in order to achieve a given structure-property relationship. The experimental and analysis strategy developed for this work will allow for the realization of a comprehensive crystallization analysis of metallic glass alloys and will help to extend the knowledge of phase competition leading to successful synthesis of BMGs.
Figure 1.1 Time-Temperature-Transformation curves for crystallization showing the critical cooling rate (dash curve for bulk metallic glass alloys and dot curve for ordinary amorphous alloys)
Figure 1.2 Relationship between the saturation magnetization properties ($J_s$) and supercooled liquid region ($\Delta T_x$) for Fe-based amorphous alloys.
2. Theoretical Background and Literature Reviews

2.1 Metallic Glass Background

Since the first discovery of metallic glass formation during continuous cooling from the molten state of the binary Au-Si alloy in 1960 [21], metallic amorphous alloys or metallic glasses have been investigated intensively. Amorphous structure and metallic bonding provide the metallic glasses with unique physical and mechanical properties that cannot be found in either crystalline metals or other non-metallic amorphous materials.

The promising attributes of metallic glasses have lead researchers to search for new alloys that would form glasses at low cooling rates, which would enable the production in bulk form. In 1969, Chen and Turnbull [22] succeeded to form amorphous spheres of ternary Pd-Cu-Si alloy with a diameter of 0.5 mm at critical cooling rates of 100 K/s to 1000 K/s. Later in 1974, Chen used suction-casting methods to form 1 mm diameter rods of Pd-Cu-Si metallic glass at cooling rate of $10^3$ K/s [23], which was the first bulk metallic glass (BMG) if one arbitrarily defines the millimeter scale as bulk. In the early 1980s, Turnbull’s group [24] successfully produced glassy ingots of Pd-Ni-P BMG with a diameter of 1 cm using a boron oxide fluxing method to purify the melt and to eliminate heterogeneous nucleation. Since the 1980s, Inoue et al. [25-29] have discovered strong glass forming multicomponent La-, Mg-, Zr-, Pd-, Fe-, Cu- and Ti-based alloys with large undercooling and low critical cooling rates of 1 K/s to 100 K/s. These properties allow an increase in time before crystallization, enabling a greater critical casting thickness (> 1 cm) by conventional molding. To date, many bulk metallic glass formers have been developed in various alloy systems [30]. It can be seen that the
BMGs were developed in the sequence beginning with the expensive metallic based Pd, Pt, and Au followed by less expensive Zr-, Ti-, Ni- and Ln-based BMGs. The much less expensive Fe- and Cu-based BMGs were the most recently developed and have attracted extensive interest. Typically BMGs are alloys with 3-6 metallic components that have a large atomic size mismatch and a composition close to a deep eutectic. They are dense liquids with small free volumes and high viscosities which are several orders of magnitude higher than those in pure metals or conventional alloy melts.

The formation, structure, and property investigations of metallic glasses have attracted increasing attention, not only for their great potential in application, but also for their fundamental scientific importance. Metallic glasses exhibit remarkable properties relative to crystalline alloys due to their unique atomic configurations. In the tightly packed glassy structure, the displacement of atoms is obstructed. Thus, the metallic glass absorbs less energy upon stress-induced deformation through damping and returns more by rebounding elastically to its initial shape. With no crystal defects, materials with excellent mechanical properties i.e. high strength, high hardness, and high yield strength are produced. The absence of grain boundaries means that the material is resistant to corrosion and wear as well as possessing soft-magnetic properties.

In addition to mechanical properties, metallic glasses such as Fe-based amorphous alloys display excellent magnetic properties. The homogeneous and isotropic character of amorphous alloys results in an absence of magnetocrystalline anisotropy energy which is the energy required to change the direction of magnetization relative to crystalline axes. A small field-induced anisotropy energy allows easy direction of magnetization to be
oriented to suit a given application [31, 32]. In addition, with no microstructural defect (e.g. grain boundaries and precipitates) on which magnetic domain walls can be pinned, magnetization by wall motion is relatively easy [33]. As a result of the lack of long range atomic order, no macroscopic magnetocrystalline anisotropy and no microstructural defects, ferromagnetic metallic glasses such as Fe and Co-based alloys are generally good soft magnetic materials with low hysteresis loss, low eddy current dissipation and high permeability. Usually, soft magnetic materials for a given application are chosen primarily for high saturation induction, high permeability and low losses over a variety of frequencies [31]. These favorable properties have been found in Fe-(Al, Ga)-(P,C,B,Si) and (Fe,Co)-Zr-B bulk amorphous alloys [34-36]. They exhibit excellent soft magnetic properties of high saturation magnetization of 0.96 to 1.15T, low coercivity of 1.1 to 6.4 A/m and high permeability of 7000 to 25000 at 1 kHz at room temperature. Therefore, substantial efforts have been made in searching of the new amorphous alloys with good soft magnetic properties and large glass-forming ability.

2.2 Characteristics of Glasses

When a liquid is cooled below its freezing temperature, the melt can be solidified into either a crystalline solid or a glass depending on its cooling rate. Figure 2.1 is a schematic representation of the requirement of cooling rates for different alloys. For ordinary amorphous alloys, curve (b) represents a cooling rate that is slower than the critical cooling rate ($R_c$) and the melt will solidify into a crystalline solid. While curve (a) corresponds to a cooling rate faster than the critical cooling rate and the liquid may pass
through the freezing range without crystallizing to become a supercooled liquid and then solidify as a metallic glass when the liquid reaches the glass transition temperature ($T_g$).

The critical cooling rate to form a glass is relatively slow for inorganic glasses ($\leq 10^{-1} \text{K/s}$). For metallic glasses, the critical cooling rate spans the range from about $10^{-1} \text{K/s}$ \cite{37} to more than $10^{9} \text{K/s}$ \cite{38} depending on the glass forming ability (GFA) of the alloy system. BMGs exhibit critical cooling rates as low as 1-100 K/s. Some excellent bulk glass formers have a GFA very close to silicate glasses. Figure 2.2 shows a comparison of GFA of various glasses \cite{30}, where $T_{rg}$ (the reduced glass transition temperature, $T_{rg} = T_g/T_l$) uses as a metric. The closer $T_{rg}$ is to unity, the better the GFA is.

At the glass transition temperature, certain important properties such as specific volume and enthalpy display changes. Figure 2.3 illustrates the change in specific volume, $V_{sp}$ ($\text{m}^3/\text{mol}$) when a liquid is cooled to form a crystalline solid or a glass. Curves (a) and (b) show schematically the specific volume of a liquid that is cooled fast enough to produce a glass. The glass transition ($T_g$) is denoted at the point where there is a change of slope. Note that the volume difference between liquid and glass as well as the glass transition temperature ($T_g$) depend on the cooling rate. Higher cooling rate results in a higher $T_g$ and larger volume difference as the comparison in curves (a) and (b) shows. A smaller cooling rate allows the sample to stay in equilibrium, i.e., the supercooled liquid state, until a lower temperature. On the other hand, curve (c) corresponds to a cooling rate slow enough to allow for crystallization and a sharp decrease in volume occurs when the liquid freezes at $T_m$. The slope of curve (c) is smaller after the liquid is transformed into crystalline solid. In contrast, there is no change before the glass
transition in the slope of curve (a) and (b) where the liquid is more rapidly cooled and becomes supercooled. At temperatures below the glass transition temperature, the slopes of both the glasses and crystallized solid curves are generally similar. The larger specific volume of glasses can be attributed to a more open structure in the glasses, which has limited short-range order. As a supercooled liquid is cooled to lower temperatures, its viscosity increases and the atoms which comprise it move more and more slowly.

The specific heat ($C_p$) as a function of temperature during cooling of a liquid is shown in Figure 2.4. When a crystalline solid is formed upon cooling from the liquid, the specific heat of the crystalline solid ($C_p^c$) decreases smoothly and continuously after the abrupt reduction at the crystallization temperature ($T_X$). On the other hand, if a glass is formed, the specific heat increases with decreasing temperature, as the melt becomes a supercooled liquid. The increase in specific heat terminates when the glass transition temperature is reached and $C_p$ falls to be approximately equal to that of the crystalline solid. The termination of the rise in $C_p^l$ represents the thermal manifestation of a continuous release of atomic degree of freedom at the glass transition temperature.

Calorimetric evidence of an increase in specific heat before crystallization is one of the most widely accepted indications of the transition from a glass to the supercooled liquid [39]. However, the absence of this calorimetric evidence does not necessarily exclude the existence of a glass. In some systems, the glass transition could be obscured by crystallization or enthalpy relaxation. In other systems, the increase in specific heat could be too small and difficult to measure. It was shown by Johari [40] that a two-step calorimetric test can be applied to examine whether the material is amorphous or
crystalline when the enthalpy of relaxation would obscure the glass transition. Chen and Spaepen have applied the analysis of isothermal annealing to assist identification of a “truly” amorphous alloy [39, 41]. X-ray diffraction was used in many studies to determine if the material is amorphous.

2.3 Glass Forming Ability Criteria

The combination of exceptional functional properties and the ability to produce bulk product forms has led to a significant number of important applications. However, these applications are limited to a restricted range of alloy systems. Further discovery, development, and application of metallic glass is limited by an understanding of the fundamental features that control glass forming ability (GFA) and thermal stability. Over time, the discovery of new and better glass formers has prompted a search for a comprehensive underlying rule for predicting the GFA based on thermodynamic, kinetic and structural properties of alloys. Inoue et al [42] have proposed three empirical rules for the achievement of large glass forming ability (GFA). These empirical rules are: (1) multicomponent alloy systems consisting of more than three constituent elements; (2) significantly different atomic size ratios above 12% among the main constituent elements; and (3) negative heats of mixing among the main constituent elements.

While the rules given above have been successful for guiding researchers into new alloy systems, prediction of the best glass forming compositions is still lacking, in part because no quickly and easily obtainable metrics for GFA are available that are always comparable between systems. One set of metrics that has been met with some
measure of success are those based upon calorimetric analysis [43-48]. While they still lack broadness in their applicability, when used within a given glass forming system do show a strong correlation to GFA [4, 49]. A schematic differential thermal analysis (DTA) trace of a glass in Figure 2.5 shows four important temperature–defined transitions which are: the melting temperature ($T_m$), the liquidus temperature ($T_l$), the glass transition temperature ($T_g$) and the crystallization temperature ($T_x$). Several GFA criteria have been based upon these transition temperatures.

Perhaps the most widely applied parameter used for indicating GFA is the reduced glass transition ratio ($T_{rg} = T_g/T_l$) proposed by Turnbull [43]. It is intuitive that the closer this $T_{rg}$ is to unity the easier glass formation should be, as less undercooling is required before transport is arrested by glass transition. Given a higher $T_{rg}$, a liquid has less time for nucleation of crystalline phases for the same cooling rate. Furthermore, classical nucleation theory [50] implies that the free energy barrier, $\Delta G^*$, to form a critical nucleus depends strongly upon the undercooling level as it is proportional to $T^{-1}(\Delta T)^2$. Therefore, a small gap between $T_g$ and the liquidus temperature indicates that a relatively small undercooling is necessary to obtain a glass thus increasing the probability for avoiding crystallization during cooling.

In keeping with the concepts from $T_{rg}$, Inoue proposed the width of the supercooled liquid region ($\Delta T_x$), which is the temperature interval between $T_g$ and $T_x$ ($\Delta T_x = T_x - T_g$) [48]. The larger the accessible supercooled liquid region, the less prone to crystallization the glass is (i.e. higher $\Delta T_x$ indicates higher GFA). Apart from these two metrics which approach the issue at hand from high temperature and low temperature
respectively, a variety of other dimensionless quantities have been devised which attempt to improve upon them. Four of these parameters are commonly referred to in the literature as: 

\[ \gamma = \frac{T_x}{T_g + T_l} \] [44], 
\[ \delta = \frac{T_x}{T_l - T_g} \] [45], 
\[ \psi = \frac{T_r g}{(T_x - T_g)T_g^{0.143}} \] [46], and 
\[ \beta = \frac{T_x T_g}{(T_l - T_x)^2} \] [47]. The last three criteria in particular have claimed a certain degree of superiority in their correlation to GFA; however, they seem to be only nominally better than \( T_{rg} \) and \( \gamma \) which are used more often. It should also be pointed out that even though a large number of physical-mathematical parameters and factors have been proposed to indicate the GFA of BMGs, none of these guidelines have been shown to be robust across glass forming systems. One easily identifiable example stems from the empirical observation that the best glass formers tend to be at off-eutectic compositions. Therefore, none of the \( T_l \) inclusive criteria would precisely predict the composition dependence of the GFA since they generally predict a maximum GFA at the eutectic composition at which \( T_l \) is a minimum [51]. Typically, the glass forming ability in bulk metallic glasses tends to increase as more elemental constituents are added to the alloy based on the assumption that larger number of components in an alloy system destabilizes competing crystalline phases which may form during cooling [52].

In addition to those metrics, electronic factors to structural stability should be employed in order to obtain a priori estimate of GFA given an alloy system. In much the same way that valence ratios between constituent atoms has been employed to predict the presence of intermetallic phases [53], the valence electron interactions in glasses may be utilized to gauge their stability. Nagel and Tauc [54, 55] treated a metallic glass as a nearly-free-electron metal and the dominant influence of conduction electrons on the
structure factors has been used to understand the stability of a metallic glass against crystallization. An amorphous solid was assumed to have a spherical Fermi surface. Addition of an alloying element with a differing number of valence electrons results in a minimum in the density of states. Depending upon the specific valence number and composition of the alloy, this minimum may lie at different positions relative to the Fermi energy. In a crystalline solid, the most stable compositions would be predicted when the Fermi energy falls at the boundary between bonding and anti-bonding energies. Similarly, the most stable amorphous solid would have the Fermi energy located at the minimum in the density of states curve. While the glass may still be metastable with respect to other crystals in the system, deviation from randomness in the atomic arrangements would change the shape of the Fermi surface and may result in an overall higher energy. Application of this criterion has successfully guided experiments in the Zr-Al-Ni system [83] where glass formation occurs along composition fields with a constant electron/atom ration of 1.5. Therefore, this criterion may be utilized to guide experiments, but it is not the only factor.

Louzguine [56] have separated factors influencing GFA as intrinsic and extrinsic factors. Intrinsic factors include a number of fundamental and derived thermal parameters ($T_g$, $T_x$, $T_l$, $T_{rg}$); physical properties such as heat capacity, thermal diffusivity and thermal expansion; compositional proximity to a deep eutectic reaction; and a topological contribution from efficient atomic packing in the atomic structure. Extrinsic factors include inclusion or dissolved impurity in the melt, mold surface quality and cleanliness, mold surface temperature, thermal conductivity of the mold, liquid metal turbulence
during solidification, and the degree of liquid metal superheat. Intrinsic factors assume that homogeneous nucleation competes with glass formation while extrinsic factors are operative when heterogeneous nucleation intervenes during solidification. Not only the intrinsic factors but also the extrinsic factors should be taken into consideration to predict an actual GFA of the alloy since the glasses with high intrinsic GFA can be significantly limited by the extrinsic factors.

While this discussion of the available metrics for glass forming ability has pointed out that no truly predictive factors currently exist, knowing the weaknesses of each of them is key to their proper use. All of these metrics were designed to guide experiments toward the regions of best GFA. Finer scale optimization of the GFA at the moment still requires empirical exploration.

2.4 Thermodynamics of Crystallization

The investigation of the crystallization behavior of metallic glasses has gained attention as an important measure of the stability of amorphous alloys. A more comprehensive knowledge of crystallization behavior may lead to successful synthesis of bulk metallic glass alloys. In addition, crystallization investigations are of interest in fundamental studies of glass formability and of the mechanisms of crystal nucleation and growth.

Crystallization of amorphous alloys generally occurs by nucleation and growth processes. A hypothetical diagram of the free energy for the various phases versus composition as shown in Figure 2.6 is often used to help understand the thermodynamics
of crystallization processes [57]. Both α and β are stable phases and γ is a metastable phase. The driving force for devitrification is the free energy difference between the glass and the appropriate crystalline phases. Depending on the composition of the amorphous alloy, there are three possible general reactions that crystallization of a metallic glass can follow: polymorphous crystallization, eutectic crystallization, and primary crystallization. Figure 2.7 illustrates these three reactions in a schematic form.

2.4.1 Polymorphous Crystallization

This type of transformation involves crystallization of the amorphous alloy without any change on composition into a supersaturated solid solution (1) or a metastable phase (2) or a stable crystalline phase (3). The supersaturated solid solution (α) formed in this reaction will decompose by subsequent precipitation reaction (1’) and the metastable phase (γ) will transform into the stable equilibrium phases in a later reaction (2’). This type of reaction requires the concentration of the amorphous alloy be close to the composition range of the supersaturated phase or the metastable phase and needs only single jumps of atoms across the crystallization front. The schematic morphology change of polymorphous crystallization of α phase (reaction1) is shown in Figure 2.7.

2.4.2 Eutectic Crystallization

This type of transformation occurs with simultaneous crystallization of two crystalline phases (reaction 4: α+γ or reaction 5: α+β) by a discontinuous reaction.
Subsequent further decomposition to $\alpha$ and $\beta$ can take place in the case of the metastable eutectic between $\alpha$ and $\gamma$. This type of reaction has the largest driving force and can occur over a large composition range including in the whole composition range between the two stable phases. In this form of crystallization, there is no difference in the overall composition across the reaction front. At the reaction front, the amorphous phase separates into two crystalline phases, thus this reaction should take more time due to the necessary diffusional partitioning of components compared to the polymorphous crystallization. The schematic morphology development of eutectic crystallization of $\alpha$ and $\gamma$ (reaction 4) is shown in Figure 2.7.

2.4.3 Primary Crystallization

Primary crystallization consists of nucleation and growth of one phase (reaction 6). During this reaction solute atoms will be rejected into amorphous matrix until the metastable equilibrium is reached. The remaining amorphous matrix can transform later or at higher temperatures by other reactions. The dispersed primary crystals ($\alpha$) formed in this reaction may act as the preferred nucleation site for the subsequent crystallization of the amorphous matrix. The schematic diagram in Figure 2.7 exhibits a primary crystallization of $\alpha$ phase (reaction 6) with the remaining amorphous matrix transforming to metastable $\gamma$ phase and subsequent further decomposition to $\alpha$ and $\beta$. 
2.5 Kinetics of Crystallization

While thermodynamics selects which phase transformations are possible during devitrification of amorphous alloys, kinetics will determine which of the possible reactions will occur and which phases will form the resulting microstructure. Whereas nucleation of primary crystallization and polymorphous crystallization are single step reactions, eutectic crystallization has been observed to be a process involving two nucleation steps. Nucleation may be homogeneous or heterogeneous and the rate may be in steady state or transient. In metallic glasses, the GFA is normally limited by heterogeneous nucleation of the undercooled liquid.

In initial analysis of the crystallization kinetics, steady state conditions have been considered in developing the kinetics model. Based on classical nucleation theory for heterogeneous nucleation, a general expression for the steady-state nucleation rate J can be represented as [58]

\[ J = \frac{\Delta G^* f(\theta)}{kT} \exp \left( \frac{-\Delta G^* f(\theta)}{kT} \right) \]  

(2.1)

Where \( k \) is Boltzmann’s constant, \( T \) is the absolute temperature, \( f(\theta) \) is a catalysis factor, with a range \( 0 \leq f(\theta) \leq 1 \). For spherical nuclei \( f(\theta) = (2 - 3\cos\theta + \cos^3\theta) / 4 \), where \( \theta \) is the contact angle between the nucleus and the catalytic substrate. The prefactor term can be expressed as [59]

\[ \Omega = \rho_s \nu \frac{\rho_s D_L}{d^2} \]  

(2.2)
Where \( \rho_s \) = available site density, \( \nu \) = attachment frequency, \( D_L \) = liquid diffusivity and \( d \) = jump distance. In many cases, \( \Omega = 10^{30}/\eta \text{ cm}^{-3}\text{s}^{-1} \) where \( \eta \) is the liquid shear viscosity given in term of liquidus temperature \( (T_L) \) and glass transition temperature \( (T_g) \) as

\[
\eta = 10^{-3.3} \exp \left[ \frac{3.34T_L}{T - T_g} \right] \quad (2.3)
\]

The activation barrier for nucleation of a spherical nucleus, \( \Delta G^* \), is obtained from classical theory as

\[
\Delta G^* = \frac{16\pi \sigma^3}{3\Delta G_v^2} \quad (2.4)
\]

Where \( 16\pi/3 \) is a geometrical factor characteristic for the formation of a spherical nucleus, \( \sigma \) is the interfacial energy between liquid and solid and \( \Delta G_v \) is the driving force for crystallization which is the free energy difference between the liquid \( (G_l) \) and crystalline state \( (G_s) \) \( (\Delta G_v = G_s - G_l) \). Naturally, bulk glass formers exhibit a low driving force for crystallization in the supercooled liquid, which results in low nucleation rates and subsequently improved GFA.

An important result of kinetic reactions is the development of kinetic transitions, which are represented by the appearance of altered microstructural morphologies (i.e. cells to dendrites) as well as the change from one product structure to another. In the development of nucleation transition, some of the key kinetic features can be examined as illustrated in Figure 2.8. A schematic representation of the temperature dependence in the nucleation rate in Figure 2.8a is shown for two reactions that could be either different nucleation sites for the same phase or nucleation of two phases. The fact that the
nucleation rate represents the probability of nucleus development indicates that there is a band of nucleation frequencies over which a reasonable probability for both mechanisms or both phases to develop can be defined. This range in nucleation frequencies translates into a temperature range over which both mechanisms can be observed in microstructure. The temperature range over which both mechanisms are apparent will translate into a band of the nucleation barrier values about the crossover point. In a transformation kinetic diagram, the range of the nucleation barrier will result in a band of times over which both structures could develop in a sample during isothermal holding as indicated in Figure 2.8c. A further consideration would allow for identification of different cooling rates or a cooling rate range to allow for the development of both structures as illustrated in Figure 2.8c. Therefore, the conditions shown in Figure 2.8 indicate the possible range where a mixed product structure may be developed. A number of examples have been reported for microstructural morphology and product structure transitions that provide an opportunity for a detailed kinetic analysis to account for the changing in kinetic mechanisms. For heterogeneous nucleation, the temperature dependence is not as strong as that for homogeneous nucleation and provides more favorable conditions for mixed product structures as observed in Ni-V [60], Fe-Cr-Mo-Y-C-B-BMG [61] and Zr-Al-Ni-Cu-Pd-BMG [62].

2.6 Effect of Relaxation on the Curie temperature

One of the characteristics of a glassy state is the capability to undergo structural relaxation, which means changes in atomic position with time that occurs when a sample
is held at temperatures close to but below $T_g$ [63]. Structural relaxation in metallic glasses is reflected in changes of many physical, chemical, and mechanical properties, i.e. density, enthalpy and specific heat, Young’s modulus, electrical resistivity, viscosity and Curie temperature [52]. The study of structural relaxation is a sensitive tool for investigation local atomic movements. The changes can be either irreversible that are connected with irreversible atomic rearrangements, or reversible, meaning that a given physical property in the equilibrium state is a unique function of the annealing temperature [64]. This means that metallic glasses are not in the lowest possible energy state immediately after their preparation; consequently, the structural relaxation may carry them into another amorphous state with lower energy. The structural relaxation behavior can be investigated by measurement of internal friction [65], energy changes [66], atomic configuration [67], ferromagnetic Curie point [68], electrical resistance [69] etc.

One important physical property of a ferromagnetic metallic glass is the Curie temperature ($T_c$), which is the temperature above which a ferromagnetic substance loses its ferromagnetism and becomes paramagnetic. H.S Chen [70] points out that the thermal enthalpy recovery and Curie temperature annealing near $T_g$ are of similar origin and are caused by structural relaxation. The kinetics of the structural relaxation appears to be governed by the first-order rate reaction. In addition, the Curie temperature is sensitive to the degree of structural relaxation. Relaxation of the atomic structure of the amorphous phase on annealing is accompanied by a release of the free volume and by a change of the mean interaction distance which determines the change in Curie temperature. Therefore,
control of structural relaxation may be important not only in optimizing a property for a particular application but also in maintaining the property through the life of the component.

The Curie temperature is measured either magnetically [71] or calorimetrically [72]. The DSC method provides both fast and accurate sample measurement of Curie temperature value together with heat treatment.

2.7 Glass Forming Ability and Type of Eutectic Coupled Zone

Due to the growth characteristics of dendrites and eutectics, eutectics can grow more rapidly than dendrites and therefore outgrow the dendrites over a large range of growth conditions [73, 74]. Whether the morphology is fully eutectic or primary crystalline plus eutectic after solidification is decided by the competitive growth criterion, which means the morphology having the highest interface temperature for a given growth rate or the highest growth rate for a given undercooling will be the one observed [75, 76]. This leads to the formation of a coupled zone for eutectic formation. The coupled zone representing the composition and growth temperature (undercooling) range is where an entirely eutectic microstructure forms. It is well known that there are two types of eutectic coupled zones: symmetric and asymmetric/skewed [73, 74]. A symmetrical coupled zone (figure 2.9a) is associated with regular eutectics, which is of the non-faceted/non-faceted type in which all the constituent phases possess low entropy of fusion (i.e. Al-CuAl₂). A symmetrical coupled zone always includes the eutectic composition and reflects the similar undercoolings of its constituents when they are primary. On the
other hand, an asymmetric/skewed coupled zone (figure 2.10a) is normally related to an irregular eutectic, which is of the non-faceted/faceted type in which one of the constituent phases possesses a higher entropy of fusion (i.e. Si in Al-Si and C in Fe-C). A skewed coupled zone is skewed towards the faceted phase due to the persistence of growth problems even at high undercooling.

Each growth morphology, primary dendrites or the eutectic, has its own relationship between growth rate and the liquid/solid interface temperature. For a system with a symmetric coupled zone, the growth temperature of the eutectic and the nearby alloys is always higher than that of the dendrite ($\alpha$ and $\beta$) (figure 2.9b), resulting in the formation of entirely eutectic microstructures. Due to the higher growth temperature of dendrites $\beta$ (or $\alpha$) in off-eutectic alloys (figure 2.9d), the microstructure of these alloys will be dendrites plus eutectic at intermediate growth rates. Fully eutectic microstructures will be obtained at extremely high growth rates due to the relative higher growth temperatures of the eutectics. For a system with an asymmetric/skewed coupled zone, the growth temperature of the eutectic for the eutectic alloy is lower than that of the dendrite ($\alpha$) when the growth rate is high enough (figure 2.10b), leading to the coexistence of dendrites ($\alpha$) and eutectic. As for the off-eutectic alloy, its microstructure will be fully eutectic at a sufficiently low cooling rates, dendrites ($\beta$) plus eutectic at an intermediate rate, fully eutectic again at a higher growth rate, and finally dendrites ($\alpha$) plus eutectic at an extremely high growth rate due to the relative growth temperatures as a function of growth rate among the three competing constituents: $\alpha$, $\beta$ and eutectic (figure 2.10d).
If the amorphous phase is treated as one of the competing phases together with eutectic, primary \( \alpha \), and primary \( \beta \), it is believed that glass will form when the glass transition temperature, \( T_g \), isotherm of the alloy is higher than the growth temperature of any crystalline phases at a critical growth rate, resulting in the formation of an amorphous phase. The glass transition temperature of the alloy does not depend on the growth rate, which is shown as a horizontal line in the growth-temperature/growth-rate diagrams (figure 2.9b and d and 2.10b and d), whereas the growth temperatures of eutectic and primary \( \alpha \) and \( \beta \) are highly dependent on the growth rate. \( T_g \) will intercept with the growth-temperature/ growth-rate curves of crystalline phases enabling the glass formation. For the eutectic alloy with symmetric coupled zone (figure 2.9b), the eutectic will be displaced by glass when the growth rate is higher than \( V'_a \), the critical growth rate for glass formation, resulting in the formation of fully amorphous phase. Below \( V'_a \), the morphology will be fully eutectic. For the off-eutectic alloy (figure 2.9d), fully amorphous structure will form only when the growth rate is higher than the critical rate, \( V_a \), as \( T_g \) has to be higher than the growth temperature of \( \beta \) dendrites. When the growth rate is higher than \( V_c \), the glass will displace the inter-dendritic eutectic and results in the formation of \( \beta \) dendrites in an amorphous matrix. On the other hand, for the eutectic alloy with asymmetric coupled zone (figure 2.10b), the eutectic will be replaced by glass at growth rate between \( V_c \) and \( V_a \) as \( T_g \) is higher than the growth temperature of the eutectic. A composite of \( \alpha \) dendrites plus glass will form. When the growth rate is higher than \( V_a \), a fully amorphous structure will form as \( T_g \) is higher than the growth
temperature of $\alpha$ dendrites. For the off-eutectic alloy (figure 2.10d), fully glass formation will be obtained when the growth rate is higher than $V'_c$.

Several parameters have been proposed to predict the glass forming ability including reduced glass transition temperature, $T_{rg}$ ($T_{rg} = T_g/T_l$) proposed by Turnbull in 1969 [43]. According to this criterion, the best glass former is always associated with deep eutectics and eutectic composition, since the eutectic is always associated with a minimum liquidus temperature. However, Tan et al [77] found that the optimum composition for glass formation in the La-Al-(Cu,Ni) pseudo ternary eutectic system was actually at an off-eutectic composition and this alloy showed a skewed eutectic coupled zone. They also found that GFA did not correlate well with the reduced glass transition temperature. In a further study [78], they have correlated the glass formation ability to the types of eutectic systems in terms of the growth kinetics of individual competitive phases including primary dendrite and eutectic versus glass formation in BMG forming alloys. It is concluded that the glass forming ability of a eutectic alloy system depends on the type of the eutectic coupled zone, i.e. symmetric or asymmetric eutectic coupled zone. For the alloy systems with a symmetric eutectic coupled zone, the best glass forming alloy is at or very close to the eutectic composition. For the alloys with an asymmetric/skewed eutectic coupled zone, the best glass forming alloys is at off-eutectic compositions. This conclusion reveals that even though the analysis described earlier is based on a binary system; the principle could be applicable to multi-component systems on which many of the bulk metallic glasses are based.
In particular, several kinds of crystalline phase could coexist in the amorphous matrix. In the alloys far from the best glass-forming alloys, composite structures (i.e., crystalline dendrites homogeneously distributing in amorphous matrix) can be obtained in a wide composition range as observed in La\(_{70}\)Al\(_{12.4}\)(Cu,Ni)\(_{17.6}\) [77]. In these alloys, even with a large primary crystalline phase, the remaining liquid can still have high enough stability to form a glass. Therefore, the competition between the growth of crystalline phases and the formation of an amorphous phase in various alloy systems is of considerable scientific interest. It has to be pointed out that one assumption for the existing treatment is that \(T_g\) should be relatively high, which implies that the value of \(T_{rg}\) should be high accordingly. (The higher the \(T_{rg}\) is, the better is the GFA. Further, it is easier to form the glass if its \(T_g\) is high. ) However, the question remains open as it can be applied to alloy systems with lower \(T_g\). In addition, two scientific problems about metallic glasses remain about which composition is the optimum for forming glasses and glass-matrix composites as well as what determines the glass-forming composition range in a given alloy system.

2.8 Effect of Metalloid in Fe-based Metallic Glasses

The superior properties of Fe-based amorphous alloys are often drastically lost by crystallization. However, the role of metallic elements on the crystallization temperature of several amorphous alloys has been widely investigated. Donald and Davies [80] found that the crystallization temperature is related to the difference in atomic sizes between solvent and solute metal. Giessen [81, 82] has observed the fact that the crystallization
temperature of amorphous uranium-based alloy is strongly dependent on the composition. These studies are mainly focused on the effect of metallic elements. Recently, several works were directed to study the influence of metalloid elements on the crystallization process of amorphous Fe-based alloys. M. Naka and T. Masumoto have examined the crystallization temperature of binary and ternary amorphous Fe-based alloys containing metalloid elements; B, C, Si, P and Ge using the differential thermal analysis [18]. They found that the addition of silicon most effectively increases the crystallization temperature of amorphous Fe-B and Fe-P alloy. In addition, Hu et al. have found that the GFA and the thermal stability of the Fe-based alloys were improved by adding small amount of multi-metalloids [5]. Suitable amount of metalloid additions can suppress the precipitation of the crystalline phases during the casting process, while further metalloid addition leads to the precipitation of another crystalline phase. It is also found that the glass transition temperature changes little with the increasing metalloids addition and the first crystallization exothermic peak is more sensitive to the metalloid content. It appears that a high metalloid content provides denser random packing in the supercooled liquid state leading to a low driving force for crystallization that enhances the stability of the glass and consequently an increase in the resistance to crystallization [83]. Therefore, the optimal amount of metalloid addition yields the highest crystallization temperature. Generally, metalloids are treated as one category since they have some chemical similarities. In other words, the role of a combination of metalloid elements on the GFA has not been clearly identified yet. A comparative study to examine effect of each
metalloid on the glass formation will provide a basic understanding for the composition design of metalloid elements in alloys.

2.9. BMGs Fabrication Methods

The major technique applied to produce metallic glasses after the early Duwez’s discovery of the Au-Si glass was rapid solidification. Currently, bulk metallic glasses can be synthesized either by solidification or by solid state processing. The first technique to prepare BMGs is water-quenching. In this method, the alloy is melted in a vacuum-sealed quartz tube and is then water-quenched. A bulk glassy Pd-Ni-Cu-P alloy of 4 cm in diameter was successfully prepared by water-quenching [84]. Another technique to synthesize BMGs involves unidirectional zone melting, arc-melting and then injection molding or suction casting into a copper mold. In addition, the melt also can be electromagnetically levitated and then cast into a copper mold. Several investigators utilized a wedge-shape copper mold casting technique as a means of determining the glass forming ability in various alloy systems since it provides a wide range of cooling rates for the same alloy composition within a single experiment run [85].

Fluxing and cyclic melting are employed to deal with the master alloys in order to remove the impurities, which induce the heterogeneous nucleation and subsequently reduce the glass forming ability. Shen and Schawarz have employed fluxing-melting and water-quenching to produce bulk glassy Fe-Ni-P-B alloy of 1 mm-diameter rods and 2 mm-diameter spheres [86].
Glass formation was also found through other processes such as mechanical alloying, diffusion induced amorphization in multilayers, ion beam mixing, hydrogen absorption, and inverse melting [83]. Mechanical milling is the solid state processing technique which does not involve any melting for amorphization. Zr-Cu-Ni-Al, Zr-Cu-Ni-Al-Ti and Zr-Ti-Nb-Cu-Ni-Al alloys have been mechanically milled and have been found to produce an amorphous phase [87-90]. In addition, great efforts to produce bulk amorphous alloys have been performed by various consolidation methods [63]. Powders have been compacted and consolidated by a variety of techniques e.g. cold-pressing followed by high-temperature sintering, cold and hot extrusion, hot isostatic pressure and injection molding.

Even though, there are several proposed processes for glass formation, formation of bulk metallic glasses by solidification is of the most interest and widely used. Furthermore, no bulk amorphous alloys exhibiting similar good soft magnetic properties such as those formed by solidification processes have been synthesized by any consolidation techniques. The processing conditions in solidification play a major role in determining the selection of specific product phases and their morphology. The flexibility in microstructure selection represents a key challenge to implementing a coherent guide to the control of processing that will permit an optimization of alloy design and secondary processing routes that may be necessary in order to achieve a given structure-property relationship. Therefore, a comprehensive crystallization analysis of glassy alloys will help to extend the knowledge of phase competition leading to successful synthesis of BMGs with remarkable properties.
Figure 2.1 A schematic Continuous Cooling Transformation diagram of several alloys with superimposed critical cooling rates.
Figure 2.2 A comparison of critical cooling rate and reduced glass transition temperature $T_{rg}$ for conventional metallic glass, BMGs, and silicate glasses [30].
Figure 2.3 A schematic representation of the specific volume change as a function of temperature during phase transformations. Glass 2 was formed with a slower cooling rate than Glass 1.
Figure 2.4 Specific heat of crystalline solid and supercooled liquid.
Figure 2.5 A schematic DTA trace of metallic glass
Figure 2.6 Hypothetical diagram of the free energy for the various phases as a function of composition. The numbers (1) to (6) correspond to crystallization reactions mentioned in the text.
Figure 2.7 Schematics illustrating morphology development of three major types of crystallization reactions in amorphous alloys. The numbers (1), (4) and (6) correspond to reactions in Figure 2.6.
Figure 2.8 Schematic illustration of the kinetic competition between two solid phases, $\alpha$ and $\beta$ phases, where different cooling rates yield different product phases. The probabilistic nature of nucleation results in a range, $\delta J$, of nucleation frequency which yields a transition temperature range, $\delta T$, and time interval, $\delta t$, for dual phase formation.
Figure 2.9 Schematic diagrams showing a symmetric eutectic coupled zone and relation to glass forming ability. (a) a eutectic system with a symmetric coupled zone; (c) glass forming and composite forming regions related to the coupled zone; the growth temperature of the constituents as a function of growth rate for the eutectic alloy (b) and for off-eutectic alloy (d).
Figure 2.10 Schematic diagrams showing an asymmetric/skewed eutectic coupled zone and relation to glass forming ability. (a) a eutectic system with a asymmetric coupled zone; (c) glass forming and composite forming regions related to the coupled zone; the growth temperature of the constituents as a function of growth rate for the eutectic alloy (b) and for off-eutectic alloy (d) [77]
3. Experimental Procedures

3.1 Material Selection

Fe-based amorphous alloys have shown a combination of unique properties such as high strength, high hardness, high corrosion resistance, and good soft magnetic property, which enable them to be capable for many engineering and industrial applications. Since the first development of melt spun Fe-B-Si amorphous ribbons four decades ago, they are still one of major soft magnetic materials because of their superior magnetic properties such as the relatively high saturation magnetization (Js) of 1.5-1.7T, good magnetic softness due to lack of intrinsic magneto-crystalline anisotropy, low material cost, and excellent productivity [91, 92]. However, the preparation of this magnetic alloy requires high cooling rates above $10^4$ K/s due to its low glass forming ability, thus restricting the thickness of amorphous alloys. Nowadays, the energy saving for conservation of environment is a critical issue and using the low magnetic core loss materials is one way to improve the energy efficiency. Thus, the amount of production of the amorphous alloys has been significantly increasing. Therefore, the realization of larger thickness amorphous alloys without decrease in Js and with a decrease in material cost should be a high priority for the amorphous alloy development.

Up to date, Fe-based amorphous alloys have been developed in various alloy systems including Fe-(Al,Ga)-(P,C,Si,B), Fe-(Co,Ni)-(Zr,Nb,Ta)-(Mo,W)-B, Fe-Co-Nb-Si-B, Fe-(Co,Cr,Al)-Zr-Mo-B-Y, Fe-Cr-Mo-Mn-C-B [7], Fe-(Co,Cr)-(Mo,Mn)-C-B-(Y, Ln) [10]. It is found that most Fe-based amorphous alloys are multi-component systems consisting of at least four constituent elements and contain 50-70 atomic percent Fe as the
major component with the remaining composition representing a suitable mixture of metalloids (more generally group B elements) and other elements such as Co, Ni, Al, Ga, Nb, Mo, Y and Cr, and refractory as well as lanthanide metals. In addition, it can be seen that nearly all Fe-based amorphous alloys contain either single or multiple metalloid additions C, B, P, Si indicating that metalloids play an important role in the formation of the amorphous structure in the Fe-based alloys. These alloys exhibit the glass transition and a large supercooled liquid region before crystallization and have a high GFA leading to the formation of BMG rods with diameters of the order of millimeter when they are prepared by copper-mold casting. However, the glass forming metal elements (i.e. Al, Ga, Nb, Mo and Y) and the magnetic elements (i.e. Co and Ni) in BMGs cause a significant decrease in the saturation magnetization which is very important for magnetic materials. In addition, the elements such as Ga, Nb, Mo, Y, Co and Ni are rare and expensive metals and Al, Nb, Mo and Y also decrease the productivity because they are easily prone to oxidation. Thus, it is attractive to avoid the use of these rare metal elements for conservation of environment and earth resource. From table 3.1, it is seen that metalloid elements are much cheaper than glass forming metals. The alloys composed of familiar elements with the excellent properties and low material cost should have a great advantage for engineering and industry.

Therefore, from superior magnetic properties, environmental conservation and material cost issues, the development of Fe-based BMGs without any metal element other than Fe and with relatively high Fe content is desired. In this study, the Fe-B-Si amorphous alloy widely utilized by industries is chosen as a base studied alloy.
Typically, the glass forming ability in bulk metallic glasses tends to increase as more elemental constituents are added to the alloy based on the assumption that a larger number of components in an alloy system destabilizes competing crystalline phases which may form during cooling [52]. Thus, if there is more than one kind of metalloid with different atomic size in the alloy, it is expected to obtain a denser random packing in the supercooled liquid than having only one kind of metalloid in the alloy, which makes the redistribution of atoms on a large range scale in cooling process difficult. Based on this assumption, another metalloid element is added to form a quaternary Fe-metalloid alloy. Phosphorous is selected as a candidate because it is a metalloid element and the substitution of P for B and Si will not significantly change the saturation magnetization. Table 3.2 shows the value of enthalpy of mixing and atomic radius of element B, Si, P and the atomic size mismatch with the Fe atom. In addition, Makino and coworkers have successfully developed a Fe-B-Si-P glassy alloy [91-93] with high magnetization of 1.5T which is comparable to 1.5-1.7T of the representative Fe-B-Si amorphous alloys. These alloys exhibit a large supercooled liquid region before crystallization and have a high GFA leading to the formation of BMG rods 2.5 mm diameters prepared by copper-mold casting. However, kinetic and thermodynamic properties of this alloy system have been left unsolved and the combination of metalloid elements on the GFA has not been clearly identified.
3.2 Sample Preparation

3.2.1 Alloy Preparation

Iron alloy ingots are prepared by repeated vacuum arc-melting the appropriate ratios of pure Fe (99.95%), premelted Fe₃P (99.5%), pure crystal B (99.5%), and Si (99.9999%) in an argon atmosphere. To ensure the environment is argon-protected, the chamber was evacuated and backfilled with argon for five times prior to alloy melting. The ingots were melted at least five times to assure complete melting and compositional homogeneity. A titanium button was melted before arc-melting the ingots to react with the residual oxygen and nitrogen inside the chamber. The composition of the alloy ingots is verified by weighing the ingot after arc-melting and electron probe analysis. The materials used are listed in Table 3.3. The Fe foil piece was folded into an envelope and pieces of boron and premelted-Fe₃P were placed inside prior to melting. This was done to minimize B and Fe₃P loss due to spattering or vaporization during melting.

3.2.2 Rapid Solidification Processing

3.2.2.1 Single Roller Melt-spinning Method

The production of amorphous and/or glassy ribbon samples is accomplished using a vacuum encapsulated single roller melt spinning facility as illustrated in figure 3.1. Approximately 5-10 grams of Fe-alloy sample is placed in a 17 mm-inside diameter cylindrical quartz crucible with 1 mm thick walls. One end of the crucible is left open for attachment to the pressurized inert gas source, while the other end is necked down to a point that is subsequently ground away to leave a ~1 mm diameter hole for liquid metal
ejection. A water-cooled RF induction coil is placed around the crucible to melt the alloy ingot for melt spinning. Melting is performed in an inert gas protected environment filled with argon and the chamber is evacuated to < 0.133 Pa with a direct drive roughing pump and then backfilled with argon. When the alloy is melted, a positive pressure of argon gas is applied to the top end of the crucible fixture to eject the molten alloy onto a copper wheel rotating at a tangential velocity of 55 m/s. Upon contact with the spinning copper wheel, the liquid metal solidifies onto 30-50 μm thick ribbon samples that are collected for thermal and structural analysis. In addition to ribbon samples, rapidly quenched droplet samples are produced as a result of intermittent discontinuous contact between the liquid alloy stream and the spinning wheel. At a particular wheel speed, the cooling rate can be estimated from

\[
\frac{dT}{dt} = \alpha V
\]

(3.1)

where \(V\) is the tangential wheel speed and constant \(\alpha\) for metallic melts is approximately 1.2X10^4 K/m. At a wheel speed of 55 m/s, the ribbons were produced corresponding to an approximate cooling rate of 6.6x10^5 K/s.

3.2.2.2 Copper Mold Casting Method

Master alloys prepared by the arc melting as described in section 3.2.1 were used to make rod samples. Rod samples with various diameters were prepared by arc melting an ingot under a titanium metal gettered environment and then an ingot was cast into a water-cooled copper mold under argon atmosphere. Figure 3.2 shows the copper mold casting apparatus.
3.2.2.3 Wedge Casting Method

The arc melt ingots were mechanically polished to remove any surface oxide layer before placing inside a quartz tube with a 1.5 mm diameter hole at the bottom. The inside of crucible was coated with a thin layer of $Y_2O_3$ to minimize chemical reactions between the melt and the crucible. The melting was performed under an argon atmosphere using the RF-induction heating using preparation and melting techniques similar to those describe for melt spinning earlier. A schematic of the operation is shown in figure 3.3a. When the alloy was completely melted, a positive pressure of argon gas was applied to the top end of the crucible fixture to force the liquid through the hole at the bottom of the crucible and subsequently into the copper mold (10 x 10 x 9 cm) with a V-shaped cavity (8 cm high, 4 cm wide with an adjustable opening angle 4-14°). The cooling of the liquid was recorded using four type-R thermocouples located at different positions in the wedge as shown in figure 3.3b. The thermocouples were connected to a computer using a PCI-DAS-TC input board (Omega Engineering) designed for temperature monitoring. The Daisy-Lab software processed the temperature data for viewing and storage. In addition, a fiberoptic sensor has been added to the wedge cast experimental setup to improve temperature response time and data acquisition rate as well as reduce electromagnetic noise sensitivity. The sensor is a 2.5 mm diameter sapphire lightpipe that transmits the emitted light from the melt through a fiberoptic cable to a control unit, which calculates the temperature of the melt based on the wavelength of the incoming light. The temperature range of the fiberoptic system is 500-2000°C.
3.3 Sample Characterization

3.3.1 X-Ray Diffraction Analysis

X-ray diffraction measurements were performed on a Philips STOE high resolution X-ray diffractometer with horizontal Bragg-Brentano geometry with Cu-K\(\alpha\) radiation at 40 kV. Data collection was performed using 0.04° step size with a 5-15 second count time on each step. The structure analysis was performed with WinXpow software that has peak refinement, matching and phase determination capabilities using the ICDD-JCPDS database.

3.3.2 Thermal analysis

3.3.2.1 Differential Scanning Calorimetry (DSC)

Continuous heating and isothermal calorimetry experiments performed on as-spun ribbons and wedge-cast tip were conducted with the Perkin-Elmer DSC-7 at a heating rate of 20°C/min. A sample size of approximately 5-10 mg was used for all standard DSC scans throughout this work. For high heating rate (80°C/min \(<dT/dt<450°C/min\)), experiments are conducted with the Perkin Elmer Diamond DSC instrument. DSC uses independently controlled platinum heaters to directly measure the amount of power necessary to maintain identical temperature profiles in both the sample and reference cells as illustrated in figure 3.4. For the experiments conducted with the Perkin Elmer DSC-7, ultra high purity argon gas at flow rate 20 ml/min is used as the purge gas. The environment surrounding the DSC-7 cell is maintained at a temperature of approximately 0°C with an ice-water bath. For Diamond DSC measurement, a stream of high purity
nitrogen at 20 ml/min was used as the purge the liquid nitrogen cooled sample cell. For each measurement, the purge gas is allowed to flow through the DSC cell for 30 minutes prior to the measurement to insure that the gas flow rate has reached an equilibrium state. The temperature and heat flow levels are routinely calibrated using pure indium, tin, zinc, and lead standard samples. A flat baseline from the onset of the calorimetry measurement through the completion of crystallization can be determined by subtracting the thermal trace of a repeated continuous heating measurement with the same sample that has been heated through the entirety of its crystallization scheme from the thermal trace of the as-solidified sample.

The extrapolated crystallization onset temperature is measured by extending a line drawn tangent to the inflection point of the initial peak slope through the baseline. The intersection of these two lines is deemed the crystallization onset temperature at a given heating rate as shown in figure 3.5. Similarly, the glass transition temperature is taken as the temperature where there is an inflection point in the endothermic onset signal during heating. The crystallization enthalpy is measured by integration of the exothermic heat flow signal starting at the crystallization onset and continuing until the heat flow signal return to its baseline.

Specific heat capacity measurements were performed using the Diamond DSC operating in Iso Step Scan mode. This method consists of multiple heat and hold operations through a temperature range. Temperature step sizes between 1 and 10K between holds were used with a heating rate of 10K/min. The heat capacity of the sample assembly (pan and sample) is obtained by tracking the total heat absorbed to bring the
temperature up to the next step, as measured after one minute of holding or the critical threshold of 0.01mW was crossed. The sample and its corresponding pan could then be compared to an empty pan heated under the same conditions in order to determine the specific heat of the sample material only.

### 3.3.2.2 Differential Thermal Analysis (DTA)

Differential thermal analysis (DTA) was performed using a Perkin-Elmer DTA7 thermal analyzer for sample characterization such as solidification path and liquidus temperature. A schematic of the sample and reference configuration in DTA7 is shown in figure 3.6. The crucibles were made of aluminum oxide. The temperatures were measured by type R thermocouples (Pt/Pt-10%Rh). The samples weighed between 10 and 30 milligrams. Sample and a high purity Al₂O₃ powder reference were heated in the separated aluminum oxide crucible in a high purity argon atmosphere. A typical DTA trace is shown in figure 3.7 illustrating the onset melting temperature (Tₘ), the liquidus temperature (Tₗ) and the freezing temperatures (Tₛ). Temperature calibration for the DTA was done by melting point measurements on pure metals i.e. Al and Au under conditions that were similar to the actual measurements.

A specific heat capacity measurement at high temperature range has been performed using a Perkin Elmer DTA-7 system. This method will termed the sapphire baseline method. The sapphire baseline method consists of identical and sequentially ordered runs of the sample in an aluminum pan, an empty pan, and a pan containing a sapphire standard. Heat evolution signals for each are obtained: \( \dot{Q}_{\text{sample}} \), \( \dot{Q}_{\text{empty}} \), \( \dot{Q}_{\text{sapphire}} \). The contribution of the empty pan can be subtracted from the sample and the sapphire.
Those portions of the run which do not include a reaction (i.e. crystallization, melting, solidification) are used. The ratio between \( \dot{Q}_{\text{sapphire}} \) and the known literature values for its specific heat is proportional to the sample specific heat, weighted by their respective masses. Finally, sample specific heat capacity can be determined as:

\[
C_{p, \text{sample}} = \frac{\left( \dot{Q}_{\text{sample}} - \dot{Q}_{\text{empty}} \right) \times m_{\text{sapphire}}}{\left( \dot{Q}_{\text{sapphire}} - \dot{Q}_{\text{empty}} \right) \times m_{\text{sample}}} \times C_{p, \text{sapphire, literature}} \tag{3.2}
\]

3.3.2.3 High Rate DTA (Upquenching)

The high rate DTA has been developed to monitor reactions at high heating rates. It consists of a resistively heated metal boat, containing the sample, as shown in figure 3.8. A thin yttria coating is applied to the boat and conditioned at temperatures above 1000°C to prevent reactions with the sample and boat material. Type K thermocouples and the fiber optic probe are used to monitor temperature. In addition, an oscilloscope has been used to improve data acquisition rate in order to capture the high heating rate response. The high rate DTA is particularly important for measuring reactions which can only take place on heating if the rate is high enough to push sample crystallization to higher temperatures or even to bypass crystallization completely.

3.3.3 Microscopy Analysis

Samples were prepared using standard metallographic techniques. Typically, samples were mounted either in Buehler conductive compound or Epo-Kwik resin and
then ground using silicon carbide grinding paper through 4000 grit (5 micron) size and finally the sample was polished with diamond suspension to 1 micron.

Microstructural observations were conducted using the optical microscopy and the scanning electron microscopy (SEM); JOEL 6100JSM SEM and LEO 982 SEM/FEM. Cross section of ribbons and bulk rod samples were etched in a solution of 1% hydrofluoric acid and 99% distilled water. The etchants were absorbed onto a cotton-tipped applicator and then samples were swabbed for 1-5 seconds. The etched sample was then immediately rinsed thoroughly with distilled water followed by ethanol.

The SEM samples were sputter coated with gold if the samples were mounted in the Epo-Kwik resin to ensure that all parts of the mount were electrically conductive. Both SEM machines are equipped with an Energy Dispersive Spectroscopy (EDS) detector for element analysis, but this system was not able to detect B. The beam was set to 15 KV of accelerating voltage. Imaging was utilized in back-scattered electron imaging mode (BSEI) to show chemical phase contrast based on the atomic number of the elements in the sample. All images were captured digitally with acquisition and marker bar placement handled by Digital Image Processing System (DIPS) image acquisition software.

### 3.3.4 Electron Probe Microanalysis (EPMA)

Compositional analysis of the studied alloy was conducted using an electron microprobe Cameca SX51 with WDS capabilities. Chemical composition is determined by comparing the intensities of characteristic X-rays from the sample material with
intensities from known composition (standards). Specific X-ray wavelengths are selected and counted by wave length dispersive spectrometry (WDS). WDS utilizes Bragg diffraction from crystals to select X-ray wavelengths of interest and direct them to gas-flow detectors. Table 3.4 lists types of crystals used to detect each element lines. The standards are prepared from the pure elements and intermetallic compound; pure Fe (99.95%), B (99.5%), Si (99.99%), Fe₃C and Fe₃P. The approximately 20 micrometer diameter electron beam is rastered across the sample or used in a spot mode to excite small phases in the sample. Counts from the sample are corrected for matrix effects (absorption and secondary fluorescence) to yield chemical compositions. The resulting chemical information is gathered in textural context.
Figure 3.1 schematic illustration of single-roller melt spinning apparatus
Figure 3.2 Copper mold casting apparatus
Figure 3.3 a) Schematic of a wedge cast apparatus

b) Schematic view of the wedge-shaped cavity in the casting mold indicating the location of thermocouples. Thermocouples (⊙ and ⚫) are located along the symmetry plane of the wedge at 10, 15, 20 and 25 mm above the tip of the wedge. The fiber-optic sensor (●) is located either 10 or 20 mm above the tip of the wedge.
Figure 3.4 Schematic diagram of the sample and reference configuration within the Perkin Elmer DSC 7 system
Figure 3.5  Schematic DSC traces illustrating calculation of crystallization onset temperature and glass transition temperature
Figure 3.6 Schematic diagram of the Perkin Elmer DTA 7 system
Figure 3.7 Typical DTA trace for a multicomponent alloy. The melting temperature ($T_m$) is defined by the first deviation from the best line. The liquidus temperature ($T_L$) is defined by the last peak temperature of the last thermal event on heating.
Figure 3.8 A schematic of the upquenching apparatus used in rapid heating experiments.

A direct gas tube helps to cool down the sample at high cooling rate.
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<th>Element</th>
<th>Form</th>
<th>Purity (metal basis)</th>
<th>Price per gram ($)</th>
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<tr>
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</table>

Table 3.1 Price lists of pure element per gram (Alfa catalog 2012)
Table 3.2 Enthalpy of mixing and atomic radius of element B, Si, P and the atomic size mismatch with the Fe atom [94-97, 123]

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic radius (Å)</th>
<th>Atomic size mismatch with Fe atom</th>
<th>Enthalpy of mixing with Fe (kJ/mol)</th>
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</thead>
<tbody>
<tr>
<td>B</td>
<td>0.9</td>
<td>27.4</td>
<td>-26</td>
</tr>
<tr>
<td>Si</td>
<td>1.02</td>
<td>17.8</td>
<td>-35</td>
</tr>
<tr>
<td>P</td>
<td>1.09</td>
<td>12.1</td>
<td>-39.5</td>
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</tbody>
</table>

Table 3.3 Materials used in alloy preparation

<table>
<thead>
<tr>
<th>Element</th>
<th>Form</th>
<th>Purity (metal basis)</th>
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<tbody>
<tr>
<td>Fe</td>
<td>Rod</td>
<td>99.95%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Fe</td>
<td>Foil</td>
<td>99.95%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
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</tr>
<tr>
<td>Si</td>
<td>Lump</td>
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</tr>
<tr>
<td>Fe₃P</td>
<td>powder</td>
<td>99.5%</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Fe₃P</td>
<td>powder</td>
<td>99.5%</td>
<td>Sigma Aldrich</td>
</tr>
</tbody>
</table>
Table 3.4 Electron microprobe crystal

<table>
<thead>
<tr>
<th>Element</th>
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</tr>
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<tbody>
<tr>
<td>Fe</td>
<td>LIF</td>
</tr>
<tr>
<td>B</td>
<td>PC1</td>
</tr>
<tr>
<td>Si</td>
<td>TAP</td>
</tr>
<tr>
<td>P</td>
<td>PET</td>
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</table>
4. Results

4.1 Assessment of Transition Temperatures

In order to extend the understanding of effect of multi-metalloid composition on amorphous phase formation and the fundamental aspects of synthesizing amorphous alloys, the systematic study of the composition dependence of the crystallization temperature, glass transition temperature, melting temperature, liquidus temperature and Curie temperature of Fe-B-Si-P alloys for varying amount of metalloid elements were carried out.

It is known that the binary Fe-B and Fe-P phase diagrams are quite similar and that the eutectic composition near Fe-rich side for these systems are all near 17 at% metalloid, while the binary Fe-Si phase stability is more complex with a peritectic composition near Fe-rich side at about 30 at% Si. Therefore, a composition range of 15-26 at% for the metalloid content is selected in this study. First, the crystallization temperature and crystallization behavior of binary Fe-B alloys; Fe_{85}B_{15}, Fe_{83}B_{17}, Fe_{79}B_{21}, Fe_{75}B_{25}, Fe_{74}B_{26}, and Fe_{72}B_{18} were studied. The alloy compositions are presented as nominal atomic percent. It was found that the crystallization reaction consists of only one exothermic peak for alloys containing more than 17 at% B with an onset over 700K. Secondly, the addition of Si into the Fe-B binary results in crystallization temperatures over 800 K for Fe_{75}B_{15}Si_{10} and Fe_{76}B_{15}Si_{9} alloys. From the literature, the Fe_{75}B_{15}Si_{10} and Fe_{76}B_{15}Si_{9} alloys exhibit relatively high saturation magnetization (J_s) of about 1.6-1.65T. Lastly, another amorphous-forming metalloid element, P, is added to the Fe-B-Si systems. The effect of substitution of P for B and Si on the amorphous forming ability for
typical Fe\textsubscript{75}B\textsubscript{15}Si\textsubscript{10} and Fe\textsubscript{76}B\textsubscript{15}Si\textsubscript{9} alloys are investigated. Figure 4.1 shows the compositional dependence of the as-quenched structure of melt-spun ribbon samples. Glassy alloys are distinguished by the presence of glass transition. Glass transitions were not observed for any Fe-Si-B ternary alloys but were observed in a wide quaternary compositional range. The as-quenched structure was examined from the air-cooled surface of the as-spun ribbon by XRD. The X-ray diffraction pattern in figure 4.2 shows a diffuse halo peak, which is characteristic of an amorphous structure.

DSC measurements of the amorphous specimens were carried out for different compositions and at a constant heating rate of 20 K/min where the thermal stability was interpreted from the associated glass transition (T\textsubscript{g}) and crystallization temperatures (T\textsubscript{x}) as shown in Figure 4.3. Transformation of an amorphous solid to a supercooled liquid is observed as an endothermic peak due to an increase in the specific heat. Wide ranges of the onset crystallization (537-576 °C) with alloy composition are observed. At levels of P above about 4 at\%, there are two distinct types of heat evolution response during crystallization. The first, as can be seen in Fe\textsubscript{76}B\textsubscript{11}Si\textsubscript{8}P\textsubscript{5} (Figure 4.3), is a broad exothermic peak which implies a slower overall reaction rate. The second, exemplified by Fe\textsubscript{74}B\textsubscript{10}Si\textsubscript{8}P\textsubscript{7} (Figure 4.3), takes place over a much narrow temperature range due to fast simultaneous crystallization of multiple phases. A graphical summary of the relevant transition temperatures observed across many compositions is given in Figure 4.4. A distinct glass transition is observed in a wide composition range and within this range we can use the temperature interval (\Delta T\textsubscript{x}) between T\textsubscript{g} and T\textsubscript{x} as a metric for glass formation ability. \Delta T\textsubscript{x} over 40K is observed in the range of 9-12 at\% B, 7.2-9 at\% Si, and 4.8-6 at\%
P, but the largest $\Delta T_x$ is 52K for Fe$_{76}$B$_{10}$Si$_9$P$_5$ and Fe$_{76}$B$_{11}$Si$_8$P$_5$. The different transition temperatures over the whole range of compositions are plotted as shown in Figure 4.4d. As seen from this figure, the glass transition, $T_g$, and the first crystallization peak, $T_{x1}$, seem to decrease with decreasing metalloid content. The corresponding onset melting temperature ($T_m$) and the offset melting temperature (liquidus temperature: $T_l$) are measured by differential thermal analysis (DTA) at heating rate of 40 K/min. Figure 4.5 shows the compositional dependence of $T_m$ and $T_l$ of as cast samples. It can be implied that the compositions of the alloys used in the present investigation are close to the eutectic composition since the melting temperature varied by only a few degrees. While the liquidus temperature seems to be decrease with either increasing P content or decreasing B content.

The as-spun ribbons were isothermally annealed at a set various temperatures including: 1) below the onset temperature of the first crystallization peak, 2) after the onset crystallization temperature, between $T_{x1}$ and $T_{x2}$, respectively, and held at the annealing temperature for a few seconds in the DSC in order to study the crystallization behavior and the evolution of the microstructure. The annealed samples were characterized by XRD. Figure 4.6 shows the x-ray diffraction pattern of Fe$_{74}$B$_{10}$Si$_9$P$_7$ ribbons heated up to 560°C with a heating rate of 40°C/min and holding times of 28, 25, and 60 seconds in order to observe the phase evolution. The first phase formed during the isothermal heat-treatment can be ascribed as indicated in figure 4.7 for each alloy composition. Only the characteristic XRD peaks of Fe$_2$B are observed in alloys containing 15 at% B. At lower boron content and near the 85% Fe+Si line, the phase
selection is more complicated. In this section, it is expected that the driving force for nucleation is quite close for the constituent phases so that kinetic competition become crucial.

As the effect of P on the crystallization behavior of Fe-B-Si amorphous alloys has been studied, the important changes in the Fe-B-Si as-spun ribbons with P addition are 1) a lower crystallization onset temperature (10-30°C), 2) a lower onset of melting (150-200°C), 3) change to a single broad crystallization peak as opposed to a multipeak crystallization reaction. The change in temperature range and the shape of the crystallization peak are related to the alteration of crystallization behavior in the metallic glass. Therefore, a more comprehensive knowledge of crystallization behavior of Fe-B-Si-P will lead to successful synthesis of BMG alloys. Depending on the alloy composition, crystallization of a Fe-B-Si-P glassy alloy can follow primary and eutectic crystallization reactions. In order to investigate the dependence of alloy composition on crystallization processes as well as the variation of kinetic transitions, two alloy compositions, Fe_{76}B_{10}Si_{9}P_{5} and Fe_{77}B_{7}Si_{7}P_{10}, are selected from inside and outside best glass forming region respectively (as shown Figure 4.4c). Continuous heating, isothermal annealing, and systematic microstructural characterization measurements are applied to analyze the kinetics of the possible reactions and resulting microstructures of the selected compositions.
Figure 4.1 Composition dependence of as-quenched structure of melt-spun Fe-B-Si-P alloys. (Glassy and Amorphous alloys are distinguished by the presence of glass transition.)

Figure 4.2 The X-ray diffraction pattern obtained from as spun ribbons at the air-cooled surface of Fe$_{76}$B$_{9.5}$Si$_{8.5}$P$_6$ alloy
Figure 4.3 DSC profiles for as quenched Fe-B-Si-P alloys for a heating rate of 20 K/min.
(a) Glass transition temperature
(b) Crystallization Temperature
(c) Compositional dependence of supercooled liquid region ($\Delta T_x$)
(d) Transition temperatures of various alloys

Figure 4.4 Compositional dependence of transition temperatures for as-spun alloy determined by DSC. The temperatures are onset temperatures (°C) which can be determined as the intersection of the tangents on the scan above and below the initial change in the baseline slope (i.e. as indicated by the arrows in figure 3.5). The heating rate was 20 °C/min.
(a) Melting temperature (°C)

(b) Liquidus Temperature (°C)

(c) Temperature interval between $T_l$ and $T_m$
Figure 4.5 The compositional dependence of (a) melting temperature, (b) liquidus temperature and (c) temperature interval between $T_1$ and $T_m$ of as cast Fe-B-Si-P alloy system. The heating rate and cooling rate were 40 °C/min.
Figure 4.6 XRD patterns of annealed samples of amorphous Fe\textsubscript{74}B\textsubscript{10}Si\textsubscript{9}P\textsubscript{7} alloy at 560°C for (a) 28 seconds, (b) 35 seconds and (c) 60 seconds.
Figure 4.7 The compositional dependence of crystalline phases controlling amorphization of Fe-B-Si-P alloys.
Figure 4.8 Enlarged DSC traces of Fe\textsubscript{74}B\textsubscript{10}Si\textsubscript{9}P\textsubscript{7}, Fe\textsubscript{76}B\textsubscript{9.5}Si\textsubscript{9}P\textsubscript{5.5} and Fe\textsubscript{77}B\textsubscript{6}Si\textsubscript{7}P\textsubscript{10}

showing T\textsubscript{c}, T\textsubscript{g} and T\textsubscript{x}
4.2 Solidification Microstructure Evolution and Transition Zone in Wedge Casting

Metallic glasses are very sensitive to change in alloy composition and process parameters that strongly affect their GFA and thereby the cooling rates required for the formation of such alloys. A wedge-shape copper mold casting technique is chosen to evaluate the GFA as it provides a wide range of cooling rates for the same alloy composition within a single experimental run. Liquid-crystalline transformation behavior during continuous cooling is examined for the representative Fe-based glass forming molten alloys, Fe\textsubscript{76}B\textsubscript{10}Si\textsubscript{9}P\textsubscript{5} and Fe\textsubscript{77}B\textsubscript{6}Si\textsubscript{7}P\textsubscript{10}, which are ejected into a wedge-shape cavity in a copper mold. Pryds et. al. [98] prepared the bulk amorphous of Mg-Cu-Y-Al alloy using a technique of rapid cooling of the melt in a copper wedge mold. The experiments were carried out both with and without water-cooling of the copper mold and the results show clearly that there is only a small effect of the water-cooling on the maximum thickness of the amorphous layer. For the present study, the mold was constructed of a rather large block of copper to make it act as a heat sink for the alloy during the short cooling-down period. In order to measure the temperature as a function of time during cooling, thermocouples were placed in the center plane of the wedge mould at different positions along the z-direction. The thickness of the thermocouple wires was 0.003 inches in order to achieve a short response time in the temperature measurements. The maximum thickness of the amorphous phase is determined for various runs. Typically, the largest amorphous thickness measured in the present investigations was ~ 0.8 mm. This is not in good accordance with the maximum diameter achieved for the same alloy produced by suction casting into a copper mould [99] due to
the difference in heat transfer dimension. The heat transfer in the wedge dominates only in the x-z plane (see figure 3.3b), while the relatively long width of the wedge (40 mm) in y plane which is considered to be semi-infinite compared to heat transfer distances (2.5 mm) in a rod. The suction casting provides a higher rate of heat extraction for a given dimension size resulting in larger amorphous thickness.

Figure 4.9 shows the final shape of the sample. The evidence of turbulent flow is seen obviously on the sample surface. This implies that extrinsic factors including the incorporation of inclusions, dissolved impurities in the melt, mold surface quality and cleanliness, mold surface temperature, thermal conductivity of the mold, liquid metal turbulence during solidification and the degree of liquid metal superheat should be taken into consideration since these factors can limit the actual GFA of the alloy [56]. In addition, from the final shape, it is obviously seen that the poor glass forming alloy (Fe_{77}B_{7}Si_{6}P_{10}) has lower viscosity than the best glass former alloy (Fe_{76}B_{10}Si_{9}P_{5}) since it can fill the mold cavity better than the best glass forming alloy does.

Figure 4.10 shows the optical and SEM micrographs in the transverse long section of the wedge Fe_{76}B_{10}Si_{9}P_{5} sample. Figure 4.11 and 4.12 show the optical and SEM micrographs in the cross section of the wedge Fe_{76}B_{10}Si_{9}P_{5} and Fe_{77}B_{6}Si_{7}P_{10} samples, respectively. It is clearly seen that the transition from glassy to crystalline phase takes place with an increase of the distance from the vertical edge or the surface contacted with the copper mold. One important observation that has been made during the analysis of wedge castings for the two representative alloys is the variety in appearance of the transition region between amorphous and crystalline as-cast microstructure as
schematically shown in Figure 4.13. The two extreme situations that have observed are identified in Figure 4.10, 4.11 and 4.12. In Fe$_{76}$B$_{10}$Si$_9$P$_2$ alloy, the approximate transition boundary band forms a V-shape while in Fe$_{77}$B$_5$Si$_7$P$_{10}$ alloy that of forms a flattened U-shape. The spherical eutectic regions seen in Figure 4.12f are surrounded by an amorphous phase which indicates that growth was arrested as the temperature fell below $T_g$ following nucleation of the solid. The evolution of the microstructure of the initially amorphous phase was examined by X-ray diffraction and differential scanning calorimetry.
Figure 4.9 The final shape of wedge cast sample of (a)-(c) Fe\textsubscript{76}B\textsubscript{10}Si\textsubscript{9}P\textsubscript{5} specimens and (d) Fe\textsubscript{77}B\textsubscript{7}Si\textsubscript{6}P\textsubscript{10} specimen.
Figure 4.10 (a) Optical micrograph (b-d) SEM micrographs taken from the region I, II, III in the transverse long section of the wedge cast Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy.
Figure 4.11 SEM micrographs taken from the selected areas in the cross section of the wedge cast Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy. (a) mixture of glassy phase and dendritic solid phases, (b)-(c) primary dendritic on the eutectic matrix, and (d) crystalline structure.
Figure 4.12 (a)-(f) SEM micrographs taken from different regions of (g) in the cross section of the wedge cast Fe$_{77}$B$_6$Si$_7$P$_{10}$ sample.
Figure 4.13 Schematic illustrations of the transition zones in (a) Fe$_{76}$B$_{10}$Si$_{9}$P$_{5}$ and (b) Fe$_{77}$B$_{6}$Si$_{7}$P$_{10}$. The imposed lines indicate the range of possible isothermal contours during cooling based on the appearance of the glass-crystalline transition region.
4.3 Phase Development and Crystallization Pathway

There is no information on the equilibrium phase diagram in Fe-B-Si-P quaternary system. In order to study the equilibrium phase, the as cast and droplet samples were analyzed via back scattered electron microscopy. These samples show Fe$_2$B as the primary phase, with three constituent phases being identified readily: α-(Fe-Si), Fe$_3$P and Fe$_3$B$_{0.63}$P$_{0.37}$. Figure 4.14 shows the SEM micrographs of as cast and droplet samples with different thermal history as described in text. From session 4.1, it was found that Fe$_{77}$B$_6$Si$_7$P$_{10}$ alloy has both lower liquidus temperature and the nearly single melting reaction and hence this alloy appears to line near the quaternary eutectic alloy composition. This presumption is also supported from the experimental results that the Fe$_{77}$B$_6$Si$_7$P$_{10}$ amorphous alloy crystallizes through a single exothermic peak. SEM micrograph in figure 4.14a also reveals the fully eutectic structure of Fe$_{77}$B$_6$Si$_7$P$_{10}$ alloy. Figure 4.14d shows the four phase eutectic structure of the as cast Fe$_{77}$B$_6$Si$_7$P$_{10}$ sample.

Two alloy compositions, Fe$_{76}$B$_{10}$Si$_9$P$_5$ and Fe$_{77}$B$_6$Si$_7$P$_{10}$, have been identified as candidates for examining the transformation kinetics and overall glass stability within the Fe-B-Si-P system. These selections single out the effect of phosphorous level, phase selection and growth mode. Figure 4.15 shows the thermal properties of an as spun ribbon with about 30 µm in thickness and the tip of the wedge with 0.3 mm in thickness of Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy. Any distinct difference in T$_g$ and T$_x$ between the DSC curves is not observed. Thus, it indicates that the tip of the wedge specimen has a glassy phase that is the same as the as-quenched ribbon. Therefore, the as-quenched ribbons of the same
composition as the BMGs were used for further detailed studies on the crystallization behavior since they can be prepared easier.

From the base Fe-B-Si alloy, substitutions of phosphorus have been shown make an impact on the crystallization behavior, depending upon the level and type of substitution. The DSC traces in Figure 4.3 show that the onset of crystallization ($T_x$) observed in Fe$_{76}$B$_{10}$Si$_9$P$_5$ during constant heating at 20 K/min is about 25K higher than that observed in Fe$_{77}$B$_6$Si$_7$P$_{10}$. The increase in crystallization onset temperature signifies a higher thermal stability for Fe$_{76}$B$_{10}$Si$_9$P$_5$ glass compared to Fe$_{77}$B$_6$Si$_7$P$_{10}$ glass. The reaction temperature for the Fe$_{77}$B$_6$Si$_7$P$_{10}$ crystallization signal is depressed perhaps indicating an increase in either its driving force or a kinetic preference to nucleate earlier.

The general shape of the crystallization signal is an important factor in determining the controlling kinetic behavior. For the Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy, the initial onset of the reaction is sharp and the heat evolution increases with increased temperature, indicating rapid nucleation and growth rates. However, after the peak the heat evolution slows and a large asymmetry is revealed. The exothermic peak of Fe$_{77}$B$_6$Si$_7$P$_{10}$ is a single broader symmetric peak which implies a slower overall reaction rate.

In order to gain more comprehensive knowledge of crystallization behavior of Fe-B-Si-P which will lead to successful synthesis of metallic glass in bulk size, the reaction pathway was studied in detail. The phases which precipitate and grow within the glass have been identified by heating the as-spun ribbons into each section of the exothermic peak (one forth, one half, two third) then quenching back to room temperature. The X-ray diffraction traces show the progress of transformation progression within a selected
region of 2θ. It was found that the phase selection is more complicated for Fe$_{76}$B$_{10}$Si$_9$P$_5$ and Fe$_{77}$B$_6$Si$_7$P$_{10}$ alloys. However, with the conjunction of the non-isothermal study and the microstructural evolution of the wedge cast specimen, the crystallization pathway from the glass can be identified. Careful analysis of microstructures at a variety of cooling rates of the wedge cast samples provides significant insight into the phase selection pathways from both the liquid and glassy states. From this study, the phases formed during the non-isothermal heat-treatment and wedge cast experiment can be ascribed as follows.

In the Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy, the Fe$_3$B dendrite grows within the amorphous matrix. With a further decrease in cooling rate, the amorphous phase was replaced by the inter-dendrite eutectic resulting in the formation of Fe$_3$B dendrite plus eutectic. The SEM micrograph (figure 4.16) of Fe$_{76}$B$_{10}$Si$_9$P$_5$ wedge cast alloy shows the Fe$_3$B phase crystal that nucleated and grew during solidification from the tip. The XRD results of the non-isothermal samples also indicate that the Fe$_3$B is the first crystallization phase. As the Fe$_3$B phase grows within the amorphous matrix, the matrix composition shifts in the Fe-B-P rich direction and Fe$_3$B, Fe$_3$P, Fe$_2$B, Fe$_3$B$_{0.63}$P$_{0.37}$ phases appear during the next crystallization event.

In the Fe$_{77}$B$_6$Si$_7$P$_{10}$ alloy, the interdendrite eutectic developed in an amorphous matrix. As the cooling rate decreases, the microstructure changed dramatically to fully eutectic with very fine spacing. As the cooling rate further decreased, the intermetallic primary phases in the inter-dendritic eutectic develop. The XRD results of the non-
isothermal samples indicate that crystallization starts with the simultaneous formation of $\alpha$-(Fe$_3$Si), Fe$_3$B, Fe$_2$B and Fe$_3$P phases.
(a) As cast structure

(b) Droplet sample of Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy after reheating through the liquidus temperature and slow cooling to room temperature with the cooling rate of 3°C/min. Enlarged micrograph on the right side reveals that the (Fe-Si) phase (gray) nucleates on the Fe$_2$B dendrite (black)
(c) Droplet samples after reheating through the melting temperature and fast cooling to room temperature with the cooling rate of 100°C/min. Then samples were isothermal annealing about 75°C below the melting temperature for 100 hours to enlarge the structure.

(d) Eutectic region showing Fe$_2$B phase (black island), (Fe-Si) phase (gray island), Fe$_3$P phase (white matrix), and Fe-B-P phase (light gray matrix)

Figure 4.14 SEM micrographs of as cast and droplet samples
Figure 4.15 DSC traces of as-aspun ribbon with about 30 µm in thickness and the tip of the wedge with 0.3 mm in a thickness of Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy.
Figure 4.16 SEM micrographs of Fe_{76}B_{10}Si_{9}P_{5} alloy shows (a) dendrites of primary phases in an amorphous matrix (b) dendrites and inter-dendrite eutectics in an amorphous matrix and (c) dendrites in a eutectic matrix
4.4 Heat Transfer Analysis and Critical Cooling Rate Range Determination

While the criteria presented in part 2.3 are important for extracting information concerning the GFA of an alloy, the critical cooling rate is perhaps the most important for transition of these alloys to real-world application [100]. It is not only a direct and straightforward measure of how stable the amorphous phase is on cooling, but also provides crucial information in a kinetic analysis, such as the development of temperature-time transformation diagram (TTT) of the alloy after initial formation. In order to evaluate the critical cooling rate for a particular system, recently, Perepezko and Hildal [85, 101] utilized a wedge casting technique using direct temperature measurement of the quenching melt in order to cover a broad range of cooling rates within a single experimental run. Combining microstructure analysis of the as-cast wedge, numerical heat transfer analysis and the experimental cooling curves, the critical cooling rate for glass formation can be established accurately. In this study, wedge cast experiments were repeated until the cooling data were in good agreement between runs as well as the finite element model.

The different appearance of the glass-crystalline transition in the two alloys under study is first considered in terms of the relative heat transfer characteristics of the two alloys; in particular a different value for the Biot number (\(Bi=hl/k\)), where \(h\) is the total heat transfer coefficient at the mold-liquid interface, \(l\) is a characteristic heat transfer distance of the order of the half-width of the wedge and \(k\) is the thermal conductivity. In figure 4.11 and 4.12, \(l\) is about 0.25 and 0.15 mm for \(Fe_{75}B_{10}Si_9P_5\) and \(Fe_{77}B_7Si_6P_{10}\) alloys, respectively. A well-defined transition can be observed in \(Fe_{75}B_{10}Si_9P_5\) sample,
which implies that Fe$_{76}$B$_{10}$Si$_9$P$_5$ has larger thermal gradients during cooling, i.e. higher Biot number than that of Fe$_{77}$B$_7$Si$_6$P$_{10}$ sample. A finite element heat transfer analysis was performed to determine the influence of changes in the Biot number on the thermal gradients across the wedge at a given vertical distance $Z$ from the tip. In order to yield a different Biot number, but similar cooling rates, the thermal conductivity ($k$) and the heat transfer coefficient ($h$) were changed. The thermal conductivity can be estimated by first identifying the appearance of the glass-crystalline transition region, i.e. flat, U-shape, or V-shape, which would indicate whether a relatively high or low Biot number is expected. Then, the values of $h$ and $k$ were adjusted to achieve good agreement with the measured cooling curves and the estimated Biot number by taking mold temperature into account. The calculated isotherms for 1 second after the Fe$_{76}$B$_{10}$Si$_9$P$_5$ melt has been poured leading to the Biot number of about 0.5 where its contours resemble the shape of the glass-crystal transition zone. A similar procedure can be applied to Fe$_{77}$B$_7$Si$_6$P$_{10}$ alloy and the Biot number of about 0.1 is obtained which yield $k$-Fe$_{76}$B$_{10}$Si$_9$P$_5$/$k$-Fe$_{77}$B$_7$Si$_6$P$_{10}$ ~5/3. Figures 4.17 and 4.18 show experimental temperature profiles acquired during the quench along with calculated cooling curves of the wedge Fe$_{76}$B$_{10}$Si$_9$P$_5$ and Fe$_{77}$B$_7$Si$_6$P$_{10}$ samples, respectively. Furthermore, the different appearance of the transitions in Fe$_{76}$B$_{10}$Si$_9$P$_5$ and Fe$_{77}$B$_7$Si$_6$P$_{10}$ also reflects the different phase selection during nucleation. The appearance of the change from one product structure to another was developed as a result of competitive nucleation between different product structures. When kinetic transitions develop due to the competitive nucleation of different product phases as well as due to a glass-crystal transition, the resulting microstructural transition will not be sharp in a
wedge sample. The probabilistic nature of nucleation transition yields a transition zone with a mixed product structure and with a gradient in relative amounts of each product phase. In this study, the transition from a completely amorphous phase to the onset of crystallization does occur over a range as indicated in figures 4.10, 4.11 and 4.12, that has an extent of about 300µm for Fe\textsubscript{76}B\textsubscript{10}Si\textsubscript{9}P\textsubscript{5} and about 200 µm for Fe\textsubscript{77}B\textsubscript{7}Si\textsubscript{6}P\textsubscript{10}. For Fe\textsubscript{76}B\textsubscript{10}Si\textsubscript{9}P\textsubscript{5}, the initial crystallization involves nucleation of a metastable Fe\textsubscript{3}B structure while a eutectic structure of α-(Fe,Si)+Fe\textsubscript{3}B initially develops in Fe\textsubscript{77}B\textsubscript{7}Si\textsubscript{6}P\textsubscript{10}.

Based on a FEHT model that aligns more closely with the experimental data and SEM results that clearly provide a transition point between glass and crystalline region of the wedge, the critical cooling rates were defined. The critical cooling rate ranges were 500-700 and 1200-1350 K/s for Fe\textsubscript{76}B\textsubscript{10}Si\textsubscript{9}P\textsubscript{5} and Fe\textsubscript{77}B\textsubscript{7}Si\textsubscript{6}P\textsubscript{10}, respectively. These values support that fact that Fe\textsubscript{76}B\textsubscript{10}Si\textsubscript{9}P\textsubscript{5} is the better glass forming than Fe\textsubscript{77}B\textsubscript{7}Si\textsubscript{6}P\textsubscript{10}. The presence of a glassy phase near the tip of the wedge was confirmed through DSC analysis (Figure 4.19) and XRD (Figure 4.20). Table 4.1 summarizes the thermal properties, the calculated critical cooling rate ranges, and the maximum glassy casting thickness. The thermal analysis was performed on samples taken from the tip of the wedge using DSC and DTA. Based upon the criteria presented in part 2.3 such as $T_{rg}$, $\gamma$, and $\Delta T_x$, it was found that these criteria still lack predictive information. $\Delta T_x$ indicates that Fe\textsubscript{76}B\textsubscript{10}Si\textsubscript{9}P\textsubscript{5} is better glass forming alloy, while $T_{rg}$, $\gamma$ indicates that Fe\textsubscript{77}B\textsubscript{7}Si\textsubscript{7}P\textsubscript{10} is better glass forming alloy. Thus, the critical cooling rate is perhaps the most practical of results pertaining to initial alloy production. In addition, the microstructural evidence indicates
difference in the crystal/glass transition that highlights the role of heat flow characteristics and product phase selection in the overall analysis of bulk glass formation.
Table 4.1: Thermal Properties, critical cooling rate range and maximum fully glassy cross section of wedge cast samples together with the calculated GFA criteria $T_{rg}$, $\gamma$ and $\delta$.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_g$ [°C]</th>
<th>$T_x$ [°C]</th>
<th>$T_m$ [°C]</th>
<th>$T_l$ [°C]</th>
<th>$\Delta T_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{76}$B$</em>{10}$Si$_9$P$_5$</td>
<td>504</td>
<td>556</td>
<td>970</td>
<td>1144</td>
<td>52</td>
</tr>
<tr>
<td>Fe$_{77}$B$_7$Si$<em>6$P$</em>{10}$</td>
<td>504</td>
<td>539</td>
<td>973</td>
<td>1056</td>
<td>35</td>
</tr>
</tbody>
</table>

$$T_{rg} = \gamma = \frac{T_x - T_g}{T_g + T_l}, \quad \delta = \frac{T_x - T_g}{T_l - T_g}$$

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$T_{rg}$</th>
<th>$\gamma$</th>
<th>$\delta$</th>
<th>CCRR</th>
<th>Fully Glassy Thickness [mm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$<em>{76}$B$</em>{10}$Si$_9$P$_5$</td>
<td>0.44</td>
<td>0.34</td>
<td>0.87</td>
<td>500-700</td>
<td>0.80</td>
</tr>
<tr>
<td>Fe$_{77}$B$_7$Si$<em>6$P$</em>{10}$</td>
<td>0.48</td>
<td>0.35</td>
<td>0.98</td>
<td>1200-1350</td>
<td>0.25</td>
</tr>
</tbody>
</table>
Figure 4.17 Measured and calculated cooling curves for wedge cast Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy. The distances indicated in the legend are measured along the z-axis from the tip of the wedge.
Figure 4.18 Measured and calculated cooling curves for wedge cast Fe$_{77}$B$_7$Si$_6$P$_{10}$ alloy. The distances indicated in the legend are measured along the z-axis from the tip of the wedge.
Figure 4.19 DSC Trace of a wedge cast Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy
Figure 4.20 XRD pattern of a wedge cast Fe$_{76}$B$_{10}$Si$_{9}$P$_{5}$ alloy at various thickness
4.5 Kinetic Analysis of the Crystallization

A wedge casting technique is used to examine the representative Fe-based glass forming alloys by combining multiple thermal probes with a measurement-based kinetic analysis of the phase selection competition and critical cooling rate condition. Describing this methodology requires a suitable model of the nucleation behavior. The onset of crystallization is defined by when a nucleation event occurs within a volume, \(V\), at a given temperature, \(T\), after a crystallization time, \(t\), by

\[
JVt = 1
\]  
(4.1)

In initial analysis of the crystallization kinetics, steady state conditions have been considered in developing the kinetics model by assuming that transient effects are not dominant above \(T_g\) in the alloys under study. By inserting equations 2.1-2.4 into (4.1), the onset time for nucleation can be expressed as

\[
\ln(t) = \Gamma + \frac{B}{T - T_o} - \ln T + \frac{C}{T \Delta G_v^2}
\]  
(4.2)

Where \(T_o\) is the temperature at which the excess configurational entropy is zero, \(B\) is constant and typically of the order \(10^3\) for a broad range of metallic glasses, \(\Delta G_v\) is the driving force for crystallization, \(C\) represents part of the nucleation barrier and is given by \(C = (16\pi/3k)\sigma^3f(\sigma)\) and a prefactor \(\Gamma\) can be expressed as \(\Gamma = \ln(3\pi a^3A/\rho s Vk)\) which is assumed to be independent of temperature and \(A\) is a constant. Rearranging equation (4.2) yields

\[
\ln(t) - \frac{B}{T - T_o} + \ln T = \Gamma + \frac{C}{T \Delta G_v^2}
\]  
(4.3)
The isothermal heat flow traces of Fe$_{77}$B$_6$Si$_7$P$_{10}$ melt spun ribbons annealed at 793K in figure 4.21 illustrates the good reproducibility of the crystallization onset time. The average onset times for crystallization are shown as a function of annealing temperature in figure 4.22 and 4.23 for Fe$_{76}$B$_{10}$Si$_9$P$_5$ and for Fe$_{77}$B$_6$Si$_7$P$_{10}$, respectively. The average onset times were used in equation (4.3) to evaluate $\Gamma$ and C for each of the representative alloys. By plotting T versus log time, a TTT curve can be obtained for a given set of viscosity parameters $B$ and $T_0$. To account for the operative kinetics of the representative alloys, a measurement-based procedure was been developed to calculate TTT curves using the results from DSC isothermal crystallization annealing of as spun ribbons as input data to determine experimentally the key kinetics parameters. The TTT diagram for Fe$_{76}$B$_{10}$Si$_9$P$_5$ (Figure 4.24): a representative of the best glass forming alloy and the TTT diagram for Fe$_{77}$B$_6$Si$_7$P$_{10}$ (Figure 4.25): a representative of a poor glass forming alloy, are assessed using the previously described method. The primary precipitation phase from the glass was a metastable Fe$_3$B based on the DSC, XRD and SEM experimental results.

As shown in figure 4.24 and 4.25, the predicted TTT curves are extremely sensitive to change in the viscosity parameters, $B$ and $T_0$; especially the high temperature portion of the transformation diagram. The constants $\Gamma$ and C were determined through a linear fit of equation (4.3) to the experimental crystallization data yielding a range of viscosity parameters. In order to narrow down the range of viscosity parameters and to identify the suitable viscosity parameters at the high temperature bound, up-quenching experiments were performed. This technique provides a sufficiently high heating rate to bypass crystallization upon heating. This high temperature data can be used in
conjunction with low temperature isothermal data to refine and extend the nucleation kinetics analysis over a wide range of temperature. Melt spun ribbons were rapidly heated either in the high rate DTA or salt bath furnace to a pre-selected temperature. As the pre-selected temperature was approached, the heating power was ramped up to a predetermined value to achieve a steady state temperature. Samples were isothermally annealed at the pre-selected temperature for various times before rapid cooling to room temperature. The temperature profile for several samples is shown schematically in Figure 4.26. A type K- thermocouple and a fiber optic sensor were used to monitor temperature and an oscilloscope was used to capture the high heating rate response. The oscilloscope and thermocouple sensors provide a measure of the time and temperature. Figure 4.27 shows the heating rate upon immersing the thermocouple in the carrier fluid. The heating rate is about 2750°C/sec which is sufficient enough to bypass the crystallization onset since the heating rate required to bypass the nose of TTT curves of the representative alloys are about 1250-1450°C/sec.

After holding as spun ribbons for various times and temperatures, different grain sizes were observed. The subsequent crystallization microstructure was studied to evaluate the onset crystallization time. The transformation from finer to coarser grains was consistent with the TTT curve bound. When the high temperature isothermal experimental data was superimposed on the TTT curve as shown in figure 4.28, the unsuitable ranges of B and T₀ were eliminated. [The red dots represent the fine grains, dark green dots represent medium grains and blue dots represent the coarse grains.] Figure 4.29 shows the refined viscosity parameters; B and T₀ values for Fe₇₆B₁₀Si₉P₅
alloy when taking the SEM micrograph characteristics into account. It was found that more than one of B and $T_0$ values can be matched with the SEM micrographs. Although the resulting fit may not be unique values of the viscosity parameters, the range of values that yields an acceptable fit with the micrographs is small. The most suitable viscosity parameters that yield an acceptable fit with micrographs were selected. The analysis of the continuous cooling transformation diagram as discussed in the next section help to decide whether the refined viscosity parameters obtained from this method are acceptable. SEM micrographs in Figure 4.30 and Figure 4.31 show the microstructure evolution after holding as spun ribbons of Fe$_{76}$B$_{10}$Si$_9$P$_5$ and Fe$_{77}$B$_6$Si$_7$P$_{10}$ for various time and temperature, respectively. The XRD patterns in Figure 4.32 show the crystallization products of Fe$_{76}$B$_{10}$Si$_9$P$_5$ samples after isothermal annealing at various temperatures. To achieve agreement between the predicted crystallization onset time and the calculated transformation kinetics, the B value was found to be 885 for Fe$_{76}$B$_{10}$Si$_9$P$_5$ and 835 for Fe$_{77}$B$_6$Si$_7$P$_{10}$ alloys and the $T_0$ value was about 686K and 690K for Fe$_{76}$B$_{10}$Si$_9$P$_5$ and Fe$_{77}$B$_6$Si$_7$P$_{10}$ alloys, respectively. The resulting TTT diagrams after refining the high temperature bound for Fe$_{76}$B$_{10}$Si$_9$P$_5$ and Fe$_{77}$B$_6$Si$_7$P$_{10}$ were shown in figure 4.33 and figure 4.34, respectively. It was found that the TTT curves constructed from the refined viscosity parameters was consistent with the continuous cooling data as measured from DTA as well as the average crystallization onset time as measured from DSC.
Figure 4.21  Isothermal DSC traces of Fe$_{77}$B$_6$Si$_7$P$_{10}$ melt spun ribbons annealed at 793K at various runs
Figure 4.22  Isothermal DSC traces of Fe$_{76}$B$_{10}$Si$_9$P$_5$ melt spun ribbons annealed at various temperatures
Figure 4.23  Isothermal DSC traces of $\text{Fe}_{77}\text{B}_{6}\text{Si}_{7}\text{P}_{10}$ melt spun ribbons annealed at various temperatures
Figure 4.24 The effects of changes in viscosity parameter, B and $T_0$, on TTT curve shape of Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy.
Figure 4.25 The effects of changes in viscosity parameter, B and $T_0$, on TTT curve shape of Fe$_{77}$B$_6$Si$_7$P$_{10}$ alloy.
Figure 4.26 Schematic illustration of the up-quenching experiment diagram
Figure 4.27 Heating rate during salt bath experiment
Figure 4.28 Superimpose the high temperature isothermal experimental data on the TTT curve along with the changing in the viscosity parameters, B and $T_0$. 
Figure 4.29 Potential viscosity parameters, $B$ and $T_0$ of Fe$_{76}$B$_{10}$Si$_6$P$_5$ alloy when taking the SEM micrograph characteristics into account
Figure 4.30 SEM micrographs show the microstructural change after holding Fe_{76}B_{10}Si_{9}P_{5} as spun ribbons at various states.
Figure 4.31 SEM micrographs show the microstructural change after holding Fe$_{77}$B$_{6}$Si$_{7}$P$_{10}$ as spun ribbons at various states.
Figure 4.32 XRD patterns after up-quenching treatment of Fe\textsubscript{76}B\textsubscript{10}Si\textsubscript{9}P\textsubscript{5} alloy
Figure 4.33 Isothermal onset times for crystallization, critical cooling rate range and the calculated TTT curve for Fe$_{76}$B$_{10}$Si$_{9}$P$_{5}$
Figure 4.34 Isothermal onset times for crystallization, critical cooling rate range and the calculated TTT curve for Fe$_{77}$B$_6$Si$_7$P$_{10}$
While the critical cooling rate is often considered in terms of the TTT diagram, it is actually necessary to base the analysis on the continuous cooling transformation diagram (CCT). To relate the measurement of isothermal crystallization kinetics to the measured critical cooling rate range, crystallization in deeply undercooled liquids is considered to be an isokinetic reaction. In the analysis of isokinetic reactions, the additivity rule can be applied to transform a TTT diagram into a CCT diagram [102]. For additive reaction behavior, the time $t_i$ spent at a particular temperature divided by the isothermal transformation time $\tau_i$ required to start the transformation at temperature $T_i$ may be considered to represent the fraction of the total transformation time consumed at that temperature. For a non-isothermal treatment, the transformation will start when the sum of all fraction transformation time equals unity which is

$$\sum_{i=1}^{n} \frac{t_i}{\tau_i} = 1$$  \hspace{1cm} (4.4)$$

Where $n$ is the number incremental steps used in describing the non-isothermal cooling path between the $T_L$ and $T_{CCT}$ where $T_{CCT}$ is defined by the onset of nucleation during continuous cooling from the liquids temperature. Generalization of equation (4.4) yields

$$\int_{t_0}^{t_{CCT}} \frac{dt}{\tau_{TTT}(T)} = 1$$  \hspace{1cm} (4.5)$$

Where $\tau_{TTT}(T)$ defined the TTT diagram, $t_0$ represents the time where $T=T_L$ and $t_{CCT}$ is the time required to initiate crystallization for a given cooling rate. The isothermal onset time for nucleation $\tau_{TTT}(T)$ is a function of temperature, so the integration limits can be transformed from $t_0$, $t_{CCT}$ to $T_L$, $T_{CCT}$ yielding
\[ \int_{T_CCT}^{T_T} \frac{dT}{\tau_{TTT}(T)R(T)} = 1 \]  

(4.6)

where R is the cooling rate, which can be taken as a constant over the temperature interval. For a given cooling rate, equation (4.6) can be solved numerically to obtain \( T_{CCT} \) where \( \tau_{TTT}(T) \) has been developed from equation (4.2). The viscosity parameters as refined from the up-quenching technique restricts the high temperature bound of the resulting \( \tau_{TTT}(T) \) as well as the critical cooling rate range as measured from the wedge casting experiment restricts the resulting CCT curve. Consequently, the resulting CCT/TTT diagrams of the representative alloys were generated. Figure 4.35 and figure 4.36 show the resulting CCT/TTT diagrams for Fe\textsubscript{76}B\textsubscript{10}Si\textsubscript{9}P\textsubscript{5} and Fe\textsubscript{77}B\textsubscript{6}Si\textsubscript{7}P\textsubscript{10} alloys, respectively. It was found that the corresponding CCT curves are consistent with the critical cooling rate ranges which imply that the viscosity parameters used to construct the TTT curves yields an acceptable fit.
Figure 4.35 Isothermal onset times for crystallization, critical cooling rate range and the calculated TTT and CCT curves for initial crystallization of the Fe₃B phase in Fe₇₆B₁₀Si₉P₅ BMG alloy.
Figure 4.36 Isothermal onset times for crystallization, critical cooling rate range and the calculated TTT and CCT curves for initial crystallization of a Fe$_3$B in Fe$_{77}$B$_6$Si$_7$P$_{10}$ alloy.
4.6. Investigation of the Effect of Structural Relaxation on the Crystallization Onset Time

In order to study the effect of structural relaxation on the crystallization behavior of the Fe-B-Si-P alloy, as spun ribbons were subjected to an isothermal annealing treatment. An annealing sequence, as schematically shown in Figure 4.37, allows the experimenter the ability treat the as-quenched material so as to achieve a reproducible isoconfigurational state that will allow for the prediction of the structural relaxation time precisely. The heating and cooling rates are 80°C/min. The thermal program can be generically described as following: the first scan (a→b) was performed to normalize the thermal history of sample by heating through the Tg to T3 (Tg<T3<Tx). After pre-annealing (d→e) at T1, the subsequent long annealing scan (g) is held at the desired annealing temperature (T2). The annealing sequence a→g was repeated for different annealing temperatures and times in order to provide different isoconfigurational states. The crystallization onset times was recorded as a function of annealing temperature and pre-annealing condition. The first set of experiment was performed on as spun ribbons of Fe76B9.5Si8.5P6 alloy. It was found that pre-annealing treatments of Fe76B9.5Si8.5P6 ribbon at T1(733K) for 120 minutes followed by annealing at T2 (773K) resulted in a longer time to crystallization than for an as spun ribbon only annealed at T2. At another desired annealing temperature T2 (778K), the difference in crystallization onset time was nearly coincident with the non-preannealed as spun ribbon since the diffusivity of the as-quenched glass and the relaxed glass are similar when the annealing temperature T2 (778K) is slightly below Tg (782K). [120 minutes annealing time was selected because
the almost steady state Curie temperature value was achieved after annealing the as spun ribbons for 120 minutes which implies that sample may be in the fully relaxed state.]

Figure 4.38 shows the dependence of crystallization onset time on annealing temperature of Fe$_{76}$B$_{9.5}$Si$_{8.5}$P$_6$ alloy. Figure 4.39 shows the X-ray diffraction profiles of Fe$_{76}$B$_{9.5}$Si$_{8.5}$P$_6$ ribbon with different thermal histories. It is evident that the pre-annealing and as-quenched samples have the same crystallization products.

Similar crystallization behavior of samples with different isothermal configuration state can be observed in the representative alloys, Fe$_{76}$B$_{10}$Si$_9$P$_5$ and Fe$_{77}$B$_6$Si$_7$P$_{10}$ as shown in Figure 4.40. At the same temperature, the isoconfiguration state ribbon does exhibit detectable crystallization signal at longer annealing time comparing to the as-quenched state ribbon. However, when samples were annealed far below $T_g$ [$T < (T_g - 10^\circ C)$], the onset crystallization signal cannot be observed in DSC trace as well as in a log scale plot since the heat evolution is low at lower annealing temperature as seen in Figure 4.22 and Figure 4.23. In order to define the onset time, the annealing treatment at various times following by X-ray measurement was performed. Consequently, the onset crystallization time range could be estimated. Figure 4.41 shows the XRD results after samples were annealed at various time at 756K. The estimated onset crystallization time was between 6000 and 7200 seconds.

The results from this study show the significant influence of structural relaxation during annealing on the crystallization onset time. Thus, when taking the structural relaxation of glasses into account, not only the transient time ($\tau_A$) but also the structural relaxation time ($\tau_R$) must be included in the kinetic model. TTT diagrams for the low
temperature range of the representative alloys, Fe_{76}B_{10}Si_{9}P_{5} and Fe_{77}B_{6}Si_{7}P_{10} after adding the isoconfigurational state onset time are shown in Figure 4.42 and Figure 4.43 respectively. It was found that the calculated TTT curves assessed using equation 4.3 did not fit the isothermal data at low temperature ranges. Since the results show a significant effect of delay time before crystallization onset, steady state conditions no longer apply below T_g. Thus, in an analysis of the crystallization kinetics, the transient nucleation condition should be considered in developing the kinetic model.
Figure 4.37 Schematic illustration of an annealing procedure
Figure 4.38 Onset crystallization time versus temperature of Fe$_{76}$B$_{9.5}$Si$_{8.5}$P$_{6}$

- Red circle: pre-annealing treatment sample at $T_1$ (733K) for 120 minutes followed by annealed at temperature indicated in the graph
- Blue square: as-quenched sample without pre-annealing
Figure 4.39 X-Ray diffraction profiles of Fe$_{76}$B$_{9.5}$Si$_{8.5}$P$_6$ alloy after

(a) Pre-annealing at 733K for 2 hrs followed by heated up to 773K for 360 minutes

(b) Annealing at 773K for 400 minutes
Figure 4.40 Onset crystallization time versus temperature of Fe$_{76}$B$_{10}$Si$_9$P$_5$ and Fe$_{77}$B$_6$Si$_7$P$_{10}$
Figure 4.41 XRD patterns after annealing Fe$_{77}$B$_6$Si$_7$P$_{10}$ ribbons at 756K for (A) 6000 (B) 7200 (C) 9000 and (D) 14400 seconds, respectively.
Figure 4.42 Isothermal onset times for crystallization of Fe$_{76}$B$_{10}$Si$_9$P$_5$ BMG alloy
Figure 4.43 Isothermal onset times for crystallization of Fe$_{77}$B$_6$Si$_7$P$_{10}$ alloy
4.7 Investigation of the Curie Temperature Relaxation Behavior

One of the most convenient properties to measure that is sensitive to relaxation is the Curie temperature ($T_c$) [103]. The variation of $T_c$ on annealing a metallic glass can be measured by differential scanning calorimetry (DSC) [72]. The DSC method provides both fast and accurate sample measurement of Curie temperature value together with heat treatment. In this work, the behavior of relaxation processes, the effect of annealing temperature and time on the Curie temperature of Fe-B-Si-P glassy alloys were studied. The thermal stability associated with glass transition ($T_g$), Curie temperature ($T_c$) and crystallization temperature ($T_x$) were examined by DSC at a heating rate of 20K/min as shown in Figure 4.8.

In order to study the effect of the relaxation on the Curie temperature, as spun ribbons of Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy were heated to different temperatures with the annealing time fixed at 5 minutes. Figure 4.44 shows curves of the Curie temperature against the annealing temperature. The results show that the Curie temperature of the Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy increases with the increase of the annealing temperature. The Curie temperature of the as-quenched sample was 682 K rising to a maximum of about 698 K. Figure 4.45 shows the curve of the Curie temperature against the annealing time for Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy for annealing temperatures of 733K and 753K. It is seen that Curie temperature increases with increasing of annealing duration and temperature. These behaviors are in agreement with the results obtained by Lingling [104], Kaevitser et al. [105] and Miguel et al. work [106], who found that the Curie temperature of the amorphous phase increases with the annealing temperature as well as with an increase in the heat treatment duration.
and achieved a new higher limit at every new annealing temperature. If the heat treatment is continued long enough, the Curie temperature of the sample approaches a constant value. The influence of heating rate on the Curie temperature was shown in figure 4.46. It can be seen that the Curie temperature slightly decreases with the increase of the heating rate. Heating through the Curie transition could itself cause relaxation. At one temperature, the glass at a high heating rate was in a less relaxed state compared to a low heating rate glass.

Structural relaxation processes in melt-spun samples annealed at various time are clearly evidenced from the DSC heating curves (Figure 4.47) that show a broad exothermic event extending from the Curie temperature up to the crystallization onset temperature. The exothermic event associated to relaxation is shifted to higher temperatures as the annealing time is increased.

The structural relaxation processes in Fe-B-Si-P alloys based on Curie temperature change derived from DSC measurement were also studied by assuming that the transition form as-quenched disordered state to an isoconfiguration state causes an enhancement of Curie temperature change. The kinetics of structural relaxation in ribbons of the Fe-B-Si-P alloy system was studied by means of annealing treatments and their subsequent effects on Curie temperature. In all cases, the Curie temperature of the amorphous phase increases upon relaxation. According to figure 4.45, at any annealing temperature $T_c$ rises rapidly at first and then levels off at an equilibrium value. The behavior of $T_c$ on annealing can be described as a relaxation provided that two relaxation times are considered. Greer and Leake [103] suggest that these two times correspond to
two distinct processes of atomic rearrangement; a fast process and a slow process. They proposed the two exponential functions to fix the experimental points. That form is

\[ P(t) = A_0 \pm \left[ A_1 \exp\left(-\frac{t}{\tau_1}\right) + A_2 \exp\left(-\frac{t}{\tau_2}\right) \right] \]  \hspace{1cm} (4.7)

Where \( P(t) \) is the measured property, \( A_0, A_1 \) and \( A_2 \) are constants, \( t \) is the annealing time, and \( \tau_1 \) and \( \tau_2 \) are characteristic relaxation times. In case of the change in Curie temperature (\( \Delta T_c \)), equation 4.7 can be rearranged to the form of

\[ \Delta T_c(t) = \sum_{i=1}^{2} A_i \left[ 1 - \exp\left(-\frac{t}{\tau_i}\right) \right] \]  \hspace{1cm} (4.8)

A plot of \( \Delta T_c \) against the annealing time at different temperatures is shown in Figure 4.48. Experimental values were fitted by exponential functions including two relaxation times. The fitting results show that the best fitted constant \( A_1 \) and \( A_2 \) values are very similar (in the range of 3-6 K) which indicates a significant contribution of the two types of relaxation mechanisms to the change in \( T_c \). The characteristic relaxation times, \( \tau_1 \) and \( \tau_2 \), are in the order of \( \sim 5 \) to \( \sim 89 \) minutes.

Zhu et al \[107\] assumed that the Curie temperature strongly depends on the changes in short range order in amorphous structure. Thus, the fast relaxation process probably corresponds to the topological rearrangement is some local regions, acting relatively fast at the measured temperature. On the other hand, the slow relaxation process could be related to the chemical short range order (CSRO) tendency which needs a higher atomic mobility available at the relatively high temperature. CSRO involves rearrangement of chemically distinct species on fixed sites. Diffusion of the constituent
elements is also necessary for the development of the chemical ordering process of the amorphous phase. As a result, the CSRO process is much slower than the topological short range order (TSRO). In addition, the experimental results reveals that the Curie temperature is more sensitive to the TSRO changes than to the CSRO ones, since $\Delta T_{c1}(\sim 11K)$ is about twice of $\Delta T_{c2}(\sim 5K)$. That is, the Curie temperature depends on the average distance between magnetic atoms, i.e. the reduction of the Fe-Fe bond distance. As the annealing temperature increases, the relaxation time decreases because an increasing atomic mobility due to higher diffusivities will allow the sample to reach a more efficient packing of atoms in a shorter amount of time.
Figure 4.44 Relationship between Curie temperature and annealing temperature for Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy.
Figure 4.45 Relationship between Curie temperature and annealing time for Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy for which the annealing temperature were kept at 733 K and 753K.
Figure 4.46 Heating rate versus Curie temperature of Fe$_{77}$B$_{6}$Si$_{7}$P$_{10}$ and Fe$_{76}$B$_{10}$Si$_{9}$P$_{5}$ alloys
Figure 4.47 DSC traces show the change in the Curie temperature and the appearance of an endothermic peak with annealing time.
Figure 4.48 Relaxation behavior of the Curie temperature of Fe$_{76}$B$_{10}$Si$_9$P$_5$ as spun ribbons during isothermal annealing at 733K and 753 K. Fitting line using two relaxation times is included.
5. Discussion

5.1 Effects of Metalloid Elements on the Glass-Forming Ability of Fe-based Alloys

It is shown in section 4.1 that the change of alloy compositions from Fe-B-Si ternary systems to Fe-B-Si-P quaternary systems causes the increase in the glass-forming ability, as is evidenced from the decrease in the critical cooling rate accompanying the increases in the supercooled liquid region ($\Delta T_x$). Therefore, it is important to investigate the reason why the partial replacement of Fe-B-Si by phosphorus causes the significant changes. It has previously been proposed [42] that the wide supercooled liquid region is obtained for multicomponent alloy with the following three empirical rules, 1) multicomponent alloy systems consisting of more than three constituent elements, 2) significantly different atomic size ratios above 12% among the main constituent elements and (3) negative heats of mixing among the main constituent elements. The atomic size of the constituent elements in the Fe-B-Si-P alloy change in the order Fe>Si>P>B [108] and the interaction among Fe, B, Si, and P elements have large negative heat of mixing [94, 123]. Therefore, the Fe-B-Si-P alloy system satisfies the three empirical rules for the achievement of large glass forming ability and the appearance of a wide supercooled liquid region. In addition, it is presumed that the large glass forming ability of Fe-B-Si-P alloy is due to retardation of the crystallization reaction resulting from the necessity of long-range redistribution of P for growth of the Fe$_3$(B,P, Si) phase as well as due to the difficulty of precipitation of the Fe$_3$B phase resulting from the large interface energy for the high degree of dense random packed structure. [Based on the heats of mixing [123], P, B and Si exhibit strong attractive bonds with Fe; consequently it is possible to form
densely packed random structures which cause an increase in the liquid-solid interface energy, leading to retardation of precipitation of a crystalline phase. The suppression is thought to cause the increase in the thermal stability of the supercooled liquid through the retardation of precipitation of crystalline phases, leading to large $\Delta T_x$, low $R_c$ and large thickness.

The binary Fe-B and Fe-P phase diagrams are quite similar and they have a eutectic composition on the Fe-rich side near 17 at% metalloid, while the binary Fe-Si phase stability is more complex with a peritectic composition on the Fe-rich side at about 30 at% Si. It is noteworthy that for the Fe-B, Fe-P and Fe-Si systems, formation of Fe$_2$B, Fe$_3$P and Fe$_2$Si relates to a peritectic reaction but the corresponding slope for the liquidus line of Fe$_2$B and Fe$_3$P is steeper than that of associated with Fe$_2$Si. Ma et al. [109] has pointed out the steeper liquidus temperature in the eutectic region is more favorable for glass formation, thus we can deduce that B and P are more favorable for glass formation in the Fe-metalloid systems from the view of the phase diagram features.

From the base Fe-B-Si alloy, substitutions of Fe-B-Si by phosphorus have been shown to have an impact on the thermal properties as well as the crystallization behavior, depending upon the level and type of substitution. Figure 5.1 to figure 5.3 show the glass transition temperature, crystallization temperature and liquidus temperature for the Fe-B-Si-P as-spun ribbons. From the corresponding temperatures given in figure 5.1 to figure 5.3, it can be seen that substitution of either B or Si by P lowers the liquidus temperature. One can expect that formation of the primary phase Fe$_2$B was suppressed as B was substituted by P, resulting in a decrease in the liquidus temperature. With the further
increase of the P content, formation of different competing crystalline phases \( \alpha \)-Fe, Fe\(_3\)P and Fe\(_3\)P\(_{0.37}\)B\(_{0.63} \) is facilitated, leading to an increase of liquidus temperature. On the other hand, substitution of B by P slightly decreases the crystallization onset temperature and then the crystallization onset temperature decreases expeditiously with further substitution of B by P. The precipitation of Fe\(_3\)P phase reduced the thermal stability of the alloy. Substitution of Fe by P increases the liquidus temperature and increases the crystallization temperature. More phases precipitate simultaneously.

Therefore, it can be noticed that the optimum range for the P concentration should be less than 10 % at which the tendency for forming all competing crystalline phases is minimized. It is of importance to point out that the lowest liquid temperature is at 10% P but the highest GFA occurs at 5% in this particular system.

As the result of the systematic investigation of competitive formation of glasses in Fe-B-Si-P alloy systems a question concerning metallic glasses emerge; which composition provides the easiest route to glass formation? When only the Fe-B-Si-P alloy system was taken into account, as shown in Figure 4.3 and 4.5, the Fe\(_{77}\)B\(_6\)Si\(_7\)P\(_{10} \) alloy has both lower melting temperature and the nearly single melting reaction and hence this alloy appears to lie near the quaternary eutectic alloy composition. Although there is no information on the equilibrium phase diagram in Fe-B-Si-P quaternary system, this presumption is also supported from the experimental results that the Fe\(_{77}\)B\(_6\)Si\(_7\)P\(_{10} \) amorphous alloy crystallizes through a single board exothermic peak when observed with thermal analysis. Fe\(_{76}\)B\(_{10}\)Si\(_9\)P\(_5 \) has the same onset of melting but there are several distinct melting reactions up until the final liquidus temperature, which is indicative of an off-
eutectic composition. As reported by Ma et al. [109], the eutectic composition is more favorable for glass formation. Thus, the Fe_{77}B_{10}Si_{7}P_{10} alloy should exhibit better glass forming ability resulting in larger size. However, the experiment results from this study shows that the Fe_{76}B_{10}Si_{9}P_{5} alloy can produce larger size which implies that the Fe_{76}B_{10}Si_{9}P_{5} alloy is the better glass forming composition even it is not right on the eutectic composition. One of the factors that determine the best glass is the glass stability. From the experimental results, it was found that \( T_g \), \( T_x \) and \( T_p \) of both studied alloys increase with the increasing of heating rate, indicating that glass transition and crystallization both have notable kinetics effects. According to the peak shifts of the heating DSC curves at different heating rates, the apparent activation energies of these characteristic temperatures can be calculated using Kissinger equation [110-113]. The activation energy is one of the most important kinetic parameters for correctly interpreting crystallization of the studied amorphous alloys as well as it is often utilized to evaluate the thermal stability inside the supercooled liquid temperature region of primary crystallization. The activation energy for crystallization under continuous heating condition could be determined using the following equation [114]

\[
\ln \left( \frac{\beta}{T^2} \right) = \left(-\frac{Q}{RT}\right) + A
\]

(5.1)

where A is a constant and R is the gas constant. In the Kissinger method, T is a specific absolute temperature corresponding to the onset crystallization temperature (\( T_x \)) or the crystallization exothermic peaks temperature (\( T_p \)) which can be measured at different heating rates (\( \beta \)). By plotting \( \ln(\beta/T^2) \) against \( 1/T \), one obtains a straight line whose slope
is \(-Q/R\), from which the activation energy for the transformation, \(Q\), can be calculated. The Kissinger plots for Fe\(_{76}\)B\(_{10}\)Si\(_9\)P\(_5\) alloy are shown in figure 5.4 and the apparent activation energies for \(Q_{\text{onset}}\), \(Q_{\text{peak}}\) are 581 and 488 kJ/mol, respectively. Figure 5.5 shows the relationship of \(\ln(\beta/T^2)\) against \(1/T\) for Fe\(_{77}\)B\(_6\)Si\(_7\)P\(_{10}\) alloy and the values of \(Q_{\text{onset}}, Q_{\text{peak}}\) are 495 and 483 kJ/mol, respectively.

It is generally known that the onset crystallization temperature is strongly associated with the nucleation process and the exothermic peak temperature is related to the growth process. Therefore, one can assume that the activation energy calculated from the onset crystallization temperature represents the activation energy for nucleation and the peak temperature indicates the activation energy for growth. Apparently, \(Q_{\text{onset}}\) is greater than \(Q_{\text{peak}}\) for both studied alloys, indicating that nucleation process is more difficult than the growth process. It can be concluded that glass formation of the studied alloys takes place under nucleation control mechanism as a clear separation in temperature between the glass transition temperature \(T_g\) and \(T_x\) was observed upon re-heating.

In addition, the activation energy of Fe\(_{77}\)B\(_6\)Si\(_7\)P\(_{10}\) alloy is always less than Fe\(_{76}\)B\(_{10}\)Si\(_9\)P\(_5\), implying that the crystallization of Fe\(_{77}\)B\(_6\)Si\(_7\)P\(_{10}\) is easier than that of Fe\(_{76}\)B\(_{10}\)Si\(_9\)P\(_5\). Time to start for crystallization was shorter for the Fe\(_{77}\)B\(_6\)Si\(_7\)P\(_{10}\) samples. A higher thermal stability of Fe\(_{76}\)B\(_{10}\)Si\(_9\)P\(_5\) is found to be consistent with higher activation energy obtained using the Kissinger analysis.
Furthermore, one important observation that has been made for the two representative alloys is the appearance of the transition region between amorphous and crystalline as-cast microstructure. In Fe\textsubscript{77}B\textsubscript{6}Si\textsubscript{7}P\textsubscript{10} alloy, the crystalline phase which precipitated from the amorphous solid has a nearly spherical morphology with a rather smooth interface, suggesting that growth of the crystalline phase takes place without significant redistribution of the constituent elements at the interface between crystalline phase and the amorphous phase. Whereas, in Fe\textsubscript{76}B\textsubscript{10}Si\textsubscript{9}P\textsubscript{5} alloy, the crystalline phase precipitated from the amorphous solid has a dendritic morphology accompanied by significant ruggedness of the interface, suggesting that redistribution of the solute element (particularly B) at the solid-liquid interface is necessary for growth of the crystallized phase. Therefore, when the crystallized structure was taken into account, the crystallization of Fe\textsubscript{77}B\textsubscript{6}Si\textsubscript{7}P\textsubscript{10} alloy exhibits faster kinetics than the Fe\textsubscript{76}B\textsubscript{10}Si\textsubscript{9}P\textsubscript{5} alloy since there is no necessity for long-range diffusion of the solute elements during the cooperative growth of the crystallized phases in the Fe\textsubscript{77}B\textsubscript{6}Si\textsubscript{7}P\textsubscript{10} alloy.

Consequently, from the crystallized structure and activation energy of crystallization points of view, the off-eutectic composition gives a best glass forming ability. This is also supported by an achievable maximum thickness of a fully glassy structure, higher crystallization onset temperature as well as lower critical cooling rate of the off-eutectic composition comparing to those of the eutectic composition. According to a long-standing GFA criterion, the reduced glass transition temperature \(T_{rg}=T_g/T_l\) [115], the deep eutectic composition is preferable for glass formation upon cooling a liquid. However, the best glass forming composition is not always at the deep eutectics as
found in Pr-(Cu, Ni)-Al [116], La-Al-(Cu,Ni) alloy [77], Ce–Al–Cu(Co,Ni) [117], Cu-Zr-Ti-Al [118], Cu-Zr-Ti [119]. Therefore, the competition between the nucleation and growth of crystalline phases and the formation of an amorphous phase in the alloy systems is more important than the alloy composition.
Figure 5.1 Variation of glass transition temperature ($T_g$), crystallization temperature ($T_x$) and liquidus temperature ($T_l$) in Fe-based alloys with the partial replacement iron by phosphorus.
Figure 5.2 Variation of glass transition temperature ($T_g$), crystallization temperature ($T_x$) and liquidus temperature ($T_l$) in Fe-based alloys with the partial replacement boron by phosphorus.
Figure 5.3 Variation of glass transition temperature ($T_g$), crystallization temperature ($T_x$) and liquidus temperature ($T_l$) in Fe-based alloys with the partial replacement silicon by phosphorus
Figure 5.4 Kissinger Plots of $\ln(\beta/T^2)$ versus $1/T$ obtained from heating DSC scan of Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy (a) crystallization peak temperature (b) onset crystallization temperature
Figure 5.5 Kissinger Plots of $\ln(\beta/T^2)$ versus $1/T$ obtained from heating DSC scan of Fe$_{77}$B$_6$Si$_7$P$_{10}$ alloy (a) crystallization peak temperature (b) onset crystallization temperature.

(a) $Q_{\text{peak}} = 483$ kJ/mol

(b) $Q_{\text{onset}} = 495$ kJ/mol
5.2 Critical Cooling Rate Range

Rapid solidification of Fe-based alloys using techniques such as melt spinning and cooling of emulsions of fine droplets in order to form different phases at various freezing rates has stimulated a considerable amount of work. An effective approach to obtain a range of cooling rates during solidification is based upon a wedge casting method. For example, by casting Fe-B-Si-B alloys into a wedge shape copper mold, a range of micromorphologies were obtained within a single ingot for each alloy composition. These microstructural transitions provide essential background for further kinetics analysis and the microstructures of samples that solidified at cooling rates close to the critical cooling rate hold important clues to the crystallization behavior.

For a wedge-cast sample, the cooling rate is monotonically decreasing along the vertical z-axis for a fixed location from the z axis. Thus, by using the normal definition of critical cooling rate, one would expect to observe a sharp transition between an amorphous structure and a crystalline structure at a fixed z-value corresponding to a unique cooling rate. However, during the analysis of wedge casting of the representative alloys, an evident transition region between amorphous and crystalline as-cast microstructures have been observed. For both alloys, the transition from glassy to crystalline phase takes place with an increase of the distance from the vertical surface contacted with copper mold. This appearance was observed in other glass-forming alloys such as Fe_{48}Cr_{15}Mo_{14}Y_{2}C_{15}B_{6} \ [61], \ Cu_{48}Ni_{8}Ti_{34}Zr_{10} \ [120], \ La_{66}A_{44}(Cu,Ni)_{20} \ [77] \ and \ Mg_{60}Cu_{30}Y_{10} \ alloys \ [98]. \ Therefore, \ based \ upon \ on \ the \ microstructure \ appearance, \ a
critical cooling rate range should be included to account for nucleation controlled behavior instead of a single critical cooling rate.

Combining microstructure analysis of the as-cast wedge, numerical heat transfer analysis and the experimental cooling curves, the critical cooling rate ranges for glass formation can be established accurately. The critical cooling rate ranges (CCRR) for cooling from \( T_1 \) to \( T_g \) for \( \text{Fe}_{76}\text{B}_{10}\text{Si}_9\text{P}_5 \) and \( \text{Fe}_{77}\text{B}_{7}\text{Si}_6\text{P}_{10} \) alloys are 500-700 and 1200-1350 K/s, respectively. These critical cooling rate ranges are defined at wedge center positions that cover the spatial extent of the crystal/glass formation competition, as determined by SEM analysis. These values indicate a moderate glass-forming ability comparing to other Fe-based glass-forming alloys, such as \( \text{Fe}_{58}\text{Co}_{6.5}\text{Mo}_{14}\text{C}_{15}\text{B}_6\text{Er}_{0.5} \) (65 K/s), \( \text{Fe}_{74.5}\text{Mo}_{5.5}\text{P}_{12.5}\text{C}_5\text{B}_{2.5} \) (100 K/s) and \( \text{Fe}_{48}\text{Cr}_{15}\text{Mo}_{14}\text{Y}_2\text{C}_{15}\text{B}_6 \) (140-190 K/s) [61,121].

It is generally believed that the glass formation ability of alloy can be scaled well by two empirical criterions. One is the reduced glass temperature \( T_{rg} \) which is proposed by Turnbull [115] and defined by the ratio of the glass transition temperature \( T_g \) to the melting temperature \( T_m \). Another one is the supercooled liquid region \( \Delta T_x \) which is suggested by Inoue [29] and defined as the difference between the kinetic crystallization temperature \( T_x \) and \( T_g \). The \( T_{rg} \) and \( \Delta T_x \) of \( \text{Fe}_{76}\text{B}_{10}\text{Si}_9\text{P}_5 \) are 0.44 and 52K, respectively, while the \( T_{rg} \) and \( \Delta T_x \) of \( \text{Fe}_{77}\text{B}_{7}\text{Si}_6\text{P}_{10} \) are 0.48 and 35K, respectively. It seems that, based upon these common thermal metrics, the glass-forming ability of the two representative alloys is predicted to be similar. However, the maximum amorphous sample thickness in a \( \text{Fe}_{77}\text{B}_{7}\text{Si}_6\text{P}_{10} \) wedge is one-third of the obtainable amorphous sample thickness in a \( \text{Fe}_{76}\text{B}_{10}\text{Si}_9\text{P}_5 \) wedge implying lower glass-forming ability of \( \text{Fe}_{77}\text{B}_{7}\text{Si}_6\text{P}_{10} \) alloy. Their
differences of glass-forming ability result from the development of kinetic transitions. When kinetic transitions develop due to the competitive nucleation of different product phases or due to a crystal/glass transition, the resulting microstructural transition is not sharp in a wedge sample. For example, in the Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy, the approximate transition boundary band forms a V-shape while in the Fe$_{77}$B$_{10}$Si$_7$P$_{10}$ alloy it forms a flattened U-shape. The probabilistic nature of nucleation yields a transition zone with a gradient in relative amounts of each mixed product phase in both representative alloys. The thermal gradients across a section of the wedge at a given distance z from the tip of the wedge were evaluated by a finite element heat transfer analysis. The contour profiles have been marked on the microstructure. It was found that the heat transfer analysis does not only reproduce the experimental cooling curves, but also can account for the microstructural features of the cast wedge, which may indicate whether gradients have been significant. The appearance of the transition does allow for a clear assignment of the thermal contours. A V-shape profile observed in Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy may be caused by a substantial difference in the local cooling rate across a horizontal plane (xy-plane) in the wedge. The microstructural evidence clearly indicates differences in the crystal/glass transition that highlights the role of heat flow characteristics and product phase selection during nucleation in the overall analysis of bulk glass formation.

5.3 Crystallization Kinetics

In initial analysis of the crystallization kinetics, steady state conditions have been considered in developing the kinetics model by assuming that transient effects are not
dominant above $T_g$ in the alloys under study. However, from part 4.6, the results show the significant influence of structural relaxation on the crystallization onset time. A similar crystallization behavior was observed in the representative alloys, although different onset times are apparent, i.e. a significant shift in time and temperature space between two studied alloys. Since the results show a significant effect of delay time before crystallization onset, steady state conditions are no longer applied below $T_g$. In contrast, the transient nucleation condition is considered in developing the kinetic model. The incorporation of the transient nucleation factor for the time dependence of nucleation rate, $J_n$, at constant temperature is expressed as [122]

$$J_n(T,t) = J_{ss}(T) \exp\left(-\frac{\tau(T)}{t}\right) \quad (5.2)$$

where $J_{ss}$ is the steady state nucleation rate and $\tau(T)$ is the delay time. Figure 5.6 shows in the TTT diagrams when time dependent kinetic behavior in amorphous phase was applied for developing of the kinetic model which $\tau(T)$ was fit to the experimental data at low temperature range of the Fe$_{76}$B$_{10}$Si$_{9}$P$_5$ alloy.

The relaxation must involve transport of the atomic species comprising the amorphous structure, and the atomic transport is in turn affected by the degree of structural relaxation. Knowledge of atomic transport processes is important in understanding structural stability both to relaxation and to crystallization. As the metallic glass is heated up through the glass transition region, the viscosity changes dramatically as the alloy relaxes into the metastable equilibrium state of the supercooled liquid. Diffusivities may be estimated by analyzing reaction kinetics in amorphous alloys. For example, the diffusion-controlled growth of crystals in a variety of metal-metalloid
glasses has been measured. The extraction of diffusion coefficients may be difficult, and, in general, the results should be treated with caution. In case of the Fe\textsubscript{76}B\textsubscript{10}Si\textsubscript{9}P\textsubscript{5} glass, it can be estimated from transient nucleation condition.

The transient time to nucleation can be expressed by equation 5.3. This represents the amount of time to move the largest clusters across the potential gradient near r* then resulting in a constant flux across the energy barrier.

$$\tau = \frac{1}{BZ^2} = \frac{8kT\sigma_{nc/g}a^4}{D\Delta G^2_{v}C_0\nu^2_a}$$ (5.3)

Where \(v_a\) is the atomic volume, \(\Delta G_v\) is the volume energy different between liquid and solid, \(k\) is Boltzmann’s constant, \(D\) is the diffusion coefficient, \(C_0\) is the initial solute concentration, \(a\) is the atomic jump distance and \(\sigma_{nc/g}\) is the interfacial energy. By understanding the delay times, the diffusion coefficient in equation 5.3 provides a refinement to the existing data. The metal and metalloid diffusivity in Fe-based glasses are remarkably close in comparison to the substitutional and interstitial rates in the crystalline iron. It appears that the metalloid atoms in metal-metalloid glasses do not diffuse interstitially but that their movements are linked to that of the metal atoms. In metal-metalloid glasses, there could be a link between \(D\) and \(\eta\) analogous to Nabarro-Herring creep, in which the viscosity is given by

$$\eta = \frac{kT d^2}{4\Omega D}$$ (5.4)

where \(D\) is the diffusion coefficient, \(\eta\) is the viscosity, \(k\) is the Boltzmann constant, \(\Omega\) is the atomic volume and \(d\) is the grain size/characteristic distance in the metallic glass. By plotting the diffusion data of Fe\textsubscript{76}B\textsubscript{10}Si\textsubscript{9}P\textsubscript{5} taken from the viscosity data using the
relationship in equation 5.4, it was found that the both $\eta$ and $1/D$ rise linearly on relaxation below $T_g$. The diffusion coefficient appears to be consistent with the kinetics of CSRO. This was supported by the change in the Curie temperature behavior when the amorphous samples were annealed at different states. As the annealing temperature increases, the relaxation time decreases because an increasing atomic mobility due to higher diffusivities will allow the sample to reach a more efficient packing of atoms in a shorter amount of time.
Figure 5.6 Isothermal onset times for crystallization of Fe$_{76}$B$_{10}$Si$_{9}$P$_{5}$ BMG alloy
6. Concluding Remarks

Applications of metallic glasses require high stability in various environments in order to ensure an acceptable lifetime. Extensive effort has been put forth in exploring new alloy compositions in attempt to create a more thermally and kinetically stable metallic glass, but careful regard to kinetic and thermodynamic properties of these evolving materials has often been avoided. In this study the crystallization kinetics has been investigated which is very important in establishing the stability of metallic glasses and helps to extend the knowledge of phase competition leading to successful synthesis of BMGs.

Differential scanning calorimeter (DSC), x-ray diffraction (XRD) and Differential thermal analysis (DTA) analyses in series of Fe-B-Si and Fe-B-Si-P glasses clearly reveal that the partial replacement of iron, boron or silicon by phosphorous causes the change in the glass-forming ability based on their thermal properties. Addition of phosphorus into Fe-B-Si alloys results in a large supercooled liquid region, over 50 K, before crystallization takes place implying that the thermal stability of the Fe-based alloys is improved by adding multi-metalloids (B, Si and P). The large glass forming ability of Fe-B-Si-P alloy is due to retardation of the crystallization reaction resulting from the necessity of long-range redistribution of P for growth of the Fe$_3$(B,P, Si) phase as well as due to the difficulty of precipitation of the Fe$_3$B phase resulting from the large interface energy for the high degree of dense random packed structure. In addition, phosphorus exhibits strong attractive bonds with Fe, Si and B, consequently it is possible to form densely packed random structures which cause an increase in the liquid-solid interface
energy, leading to retardation of precipitation of a crystalline phase. The optimum P concentration with the best glass forming composition can be identified as Fe$_{76}$B$_{10}$Si$_9$P$_5$.

Through systematic study of the crystallization behavior in two representative alloys, the crystallization temperature of the poor glass forming alloy is much lower than that of the best glass former alloy which implies that its nucleation kinetics is faster. The first crystalline phase in the poor glass forming alloy composition which precipitated from the amorphous solid has a nearly spherical morphology with a rather smooth interface; whereas the first crystalline phase precipitated in the best glass forming alloy composition has a dendritic morphology accompanied by significant ruggedness of the interface. Since there is no necessity for redistribution of the constituent elements at the interface between crystalline phase and the amorphous phase in the poor glass forming alloy composition, the crystallization of this composition is easier than that of the best glass forming alloy composition even the poor glass forming alloy composition appears to line near the quaternary eutectic alloy composition and it exhibits the eutectic crystallization reaction. Thus, eutectic reactions do not always yield the most favorable conditions for glass formation.

The phase selection information of two representative alloys was folded into a kinetic analysis model. The heat flow analysis, the temperature measurement of the quenching melt and microstructural transitions during solidification from the wedge cast experiment provides information crucial to the development of a predictive TTT and CCT curves as well as the critical cooling rate. The critical cooling rate range provides a valuable constraint on the assignment of kinetics parameter values. For the two
representative glass-forming alloys, the crystal/glass transition has been observed to occur over a spatial range and a cooling rate interval rather than as a sharp change. The upquenching and isothermal annealing at high temperature range data provides a line of onset crystallization times to constrain the upper part bound of the TTT curve. The isothermal annealing and continuous heating data in the low temperature range provides a line between the onset crystallization time of the TTT curve and the associated CHT curve. Throughout the experiments and systematic analysis, a complete kinetic model was developed.

Furthermore, in dealing with amorphous materials, it must be remembered that initial quenched microstructures are not the only means for adjusting the properties. The thermal history of a glass can change the properties of the glass (e.g. diffusion, Curie temperature). Structural relaxation in metallic glasses annealed below the glass transition region provides insight into transient effects on the crystallization onset.
7. Future Works

For achieving larger bulk sample size, it is essential to remove or to deactivate heterogeneous nucleation sites in order to develop large undercooling. An effective method of melt conditioning for nucleant removal is based upon flux treatments [14, 86, 124] Suitable fluxing agents for iron-based alloys might be a dehydrated B$_2$O$_3$ and Pyrex glass. A preliminary study was performed on Fe$_{76}$B$_{10}$Si$_9$P$_5$. A small droplet was placed in fuse silica tube together with anhydrous B$_2$O$_3$. The silica tube was evacuated and heated to melt and purify the alloy. The tube was then quenched into water. It was found that a glassy droplet cannot be obtained by this technique for the studied alloys. According to Wilde et al [125, 126], multiple thermal cycling treatment of a sample encased in Pyrex glass helps to purify the melt by removing oxides and other crystalline inclusions which may act as heterogeneous nucleation centers during the undercooling of the melt. Therefore, freezing/heating thermal cycles of the Fe$_{76}$B$_{10}$Si$_9$P$_5$ alloy encased in either anhydrous B$_2$O$_3$ or Pyrex glass using the DTA-7 instrument was performed to investigate the undercooling. After the first 50 undercooling cycles, the maximum accessible undercooling is 90K by the use of Pyrex as a flux. The sample was wetted well by Pyrex and the sample was encased entirely. However, discoloration of the Pyrex glass was observed indicating a reaction between the Pyrex flux and sample. In contrast, a sample was not dissolved in the B$_2$O$_3$ flux under argon atmosphere in a DTA and the color of the B$_2$O$_3$ flux does not change. Thus, the next step in the assessment of higher undercooling is searching for non-react fluxing agents and suitable control environment and then repeating the thermal cycles until the steady state undercooling will be obtained. After the
melt achieves a steady state undercooling, then the sample will be transferred to the furnace. With the uses of a suitable fluxing agent and the thermal cycle treatment, larger bulk sample sizes can be produced.

Another set of experiments that may prove useful is the measurement of viscosity of the studied alloys. The measured viscosity can be used to obtain the unique values for B and T_0 which will yield a better fit for the transformation kinetics. Furthermore, the viscosity parameters will verify the results from the up-quenching experiments.

Additionally, the onset crystallization at temperatures a far below from T_g could be estimated more accurately by investigating the crystallites present in a sample using Transmission electron microscopy (TEM). Even though the TEM sample preparation is time consuming comparing to the XRD sample preparation, the TEM is more precise to identify nanocystal features which cannot be detected in the XRD.

The addition of P in Fe-B-Si based alloys has effectively improved the glass-forming ability but the cost of Fe_3P is high compared to Fe_3C. In a further study, it would be of interest to investigate the glass forming ability of Fe-B-Si-C alloys. Since the atomic radius of C is the smallest in comparison to the atomic radius of other metalloids, a large size mismatch could likely lead to more efficient packing. In preliminary work, it was found that amorphous ribbons could be obtained in Fe_{76}B_{10}Si_9C_5, (Fe_{0.75}B_{0.15}Si_{1.0})_{92.5}C_{7.5} and (Fe_{0.75}B_{0.15}Si_{1.0})_{95}C_{5} but none of them can be produced in bulk size. A systematic study of the composition dependence of glass formation in Fe-B-Si-C alloys for varying amount of metalloid elements may provide a new low cost Fe-
metalloid BMG which would yield a great advantage for the transition to commercial applications when material cost is a critical issue.
8. References

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